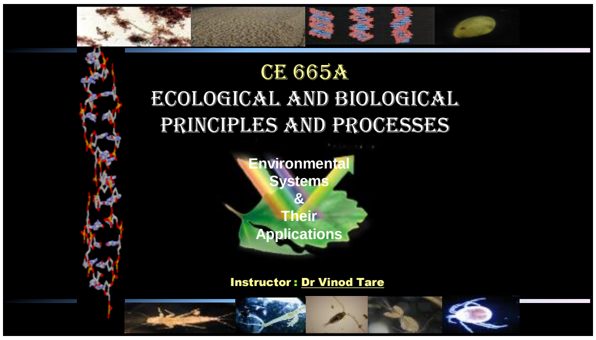


Environmental Systems – Description and Design

- **All physical, chemical and biological processes occur in some space, defined by certain boundaries**
  - The boundaries could be real/physical
  - Or the boundaries could be imaginary
  - Or some boundaries could be real and some imaginary.
- **The enclosed space is referred as Reactor**
  - Which may have certain **Inputs**
  - Certain **Outputs**, and
  - In which certain **Processes** (Physical, Chemical & Biological**) take place**
- **A reactor can also be viewed as a system.**
- **Understanding such Environmental systems, and describing and designing such systems, is the work of Environmental Professionals**

Environmental Systems – Description and Design

- **All physical, chemical and biological processes have two dominant characteristics by which they can be commonly identified and quantified**
  - First → the amount of energy available to make them occur, and the
  - Second → the speed or rate at which that energy is exercised to effect change
- **Depends on many things**
  - The numbers (masses) and the reactivities (or stabilities) of the "Energy Rich" and "Energy Poor" partners of a process
  - Pathways available to these partners for effecting their interaction in the context of a given system.

Environmental Systems – Description and Design

Specifically, all environmental processes depend upon

i. the availability of energy
ii. the means of that energy to be exercised in the timeframe of interest, and
iii. a system of such spatial and physical characteristics that it allows the reactant to "communicate" for purpose of reaction.

These are the three tenets of environmental systems

Environmental Systems – Description and Design

For successful description and/or designs of such systems, these tenets must be

1. understood based on fundamental principles
2. represented rigorously in the functional forms, and
3. integrated accurately with the functional forms of other governing principles in appropriate system models

Environmental Systems – Description and Design

In complex systems, empiricism and judgment are required to bridge gaps in absolute knowledge

- It is therefore often necessary that we make assumptions/idealizations in applying above tenets.
- If we understand the functions and constraints embodied in the principles involved, our assumptions will be rational.

Objective of this Section of the Course

To develop an appreciation of the identifying features and important characteristics of environmental systems and processes that must be factored into their analysis, modeling, and design.

Environmental Systems – Description and Design

Environmental Processes

Engineers and scientists who deal with environmental systems are ultimately concerned with changes that result from processes occurring within them

Example:

(i) Acidification of rainfall by power plant emissions
(ii) Removal of SO_x from power house emissions by wet limestone scrubbing
(iii) Contamination of groundwater and subsurface soil by seepage from land fills
(iv) Removal of contaminants using activated carbon
(v) Consumption of DO by microbes in rivers and lakes
(vi) Reduction of BOD (organic matter) of wastewater in a biological treatment process prior to discharge to a receiving water

Environmental Systems – Description and Design

Total of only three fundamentally different processes

- Phase transfer (gas-liquid) and acid base reactions in the first two examples (**Acidification of rainfall by power plant emissions and removal of SO_x from power house emissions by wet limestone scrubbing**)
- Phase transfer (liquid-solid) reaction in the second two (**Contamination of groundwater and subsurface soil by seepage from land fills; and removal using activated carbon)**
- Biological oxidation-reduction in the last two **(Consumption of DO by microbes in rivers and lakes; and reduction of BOD of wastewater in a biological treatment process prior to discharge to a receiving water)**

Important to Note:

- The point to be emphasized is that environmental systems are virtually limitless in numbers, but change is controlled by a relatively small number of fundamental processes
- The approaches we take to characterize and analyze processes are in most regards similar for natural and engineered system

Environmental Systems – Description and Design

Environmental Systems

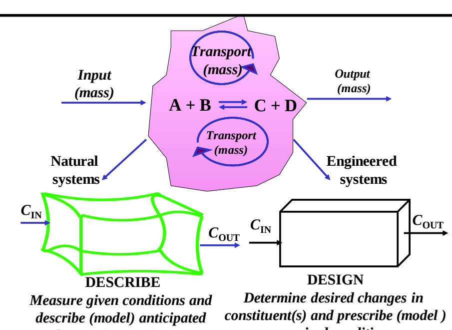
- Broad Categories
  - Natural
  - Engineered
- Scales
  - Spatial
  - Temporal

Let us first consider the similarities and differences between two broad categories of environmental systems, natural and engineered, and then address the temporal and spatial scales associated

Environmental Systems – Description and Design

Environmental Systems

- Natural
  - We are concerned with understanding and describing changes
- Engineered
  - We are concerned with the selection of conditions required to effectively accomplish specific changes



Environmental Systems – Description and Design

Natural & Engineered - Environmental Systems

- While the objectives, information requirements and expected results for natural and engineered systems are usually quite different, the underlying processes and principles of change are essentially the same. Similarly, the methods by which the processes are analyzed and described should be fundamentally the same.
- Successful approaches to system characterizations, process analyses, and quantification of components and constituent changes must in every instance, be based on the same principles and precepts of process dynamics.

Environmental Systems – Description and Design

Character and Scale

At the most elementary level we distinguish the character of a system on the basis of its scale. By character we mean the properties of a system and the nature of changes that occur within it. By scale we mean the size (spatial scale) of the system and the time (temporal scale) that together determine the boundaries within and over which the changes of interest occur

Environmental Systems – Description and Design

- The underlying goal is to understand the cause of change in any system
- Change in natural systems often occurs in a uncontrolled manner
- Alternatively, change in engineered systems is usually controlled to accomplish specific results
- Each process is modified in extent and effect by the nature of the system in which it occurs
- For example, microbial action of BOD exertion in biological treatment plant is rapid and efficient than in river or lake

A number of processes common to a verity of environmental systems, can be identified and need to be described.

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of Reaction(s)	Mass Transfer	Engineered	Natural
Absorption by Liquids	Gas/liquid mass transfer and dissolution of molecular oxygen	Molecular diffusion of O_2 at air water interface	Aeration to provide DO in biological treatment systems (e.g. ASP)	Dissolution of atmospheric O_2 in lakes, streams, estuaries, etc.

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of Reaction(s)	Mass Transfer	Engineered	Natural
Adsorption by Solids	Interactions and accumulation of solutes at solid surfaces	Interfacial and intra-particle diffusion of dissolved solutes	Removal of organic contaminants by Activated Carbon in water/ wastewater Treatment Systems	Adsorption of organic contaminants from groundwater by soils/sediments

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of Reaction(s)	Mass Transfer	Engineered	Natural
Biochemical Transformation	Enzyme mediated transformations of chemical species by electron transfer	Diffusion of substrates, nutrients, and metabolic products across microbial cell walls	Degradation of organic contaminants in biological treatment systems	Biochemical Oxygen Demand (BOD) exertion in receiving waters

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of Reaction(s)	Mass Transfer	Engineered	Natural
Chemical Transformations	Phase transformation of chemical species by electron transfer reactions	Molecular diffusion of reacting species in quiescent systems and zone of stagnation	Oxidation of organic matter (cpds) by ozone in contaminated surface or subsurface water supplies	Oxidation of dissolved organic matter (contaminants) in surface waters by photo-chemically generated free radicals

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of Reaction(s)	Mass Transfer	Engineered	Natural
Chemical Precipitation	Phase Transformation of chemical species by coordination/ partner exchange reaction	Interfacial and intra-particle diffusion associated with crystallization and particle growth phenomenon	Removal of heavy metals and phosphates in wastewater treatment and hardness ions (e.g. Ca^{++}, Mg^{++}, etc.) in water treatment	Iron oxide deposition at wetted interfaces and deposition of calcium carbonates and magnesium silicates on submerged surfaces

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of Reaction(s)	Mass Transfer	Engineered	Natural
Coagulation	Modifications of particle surface and near surface chemistry to reduce particle-particle repulsions	Molecular diffusion of dissolved species into particle double layers and to particle surfaces	Destabilization of SS by inorganic coagulants or inorganic poly-electrolytes in water/wastewater treatment	Destabilization of colloids by natural salts in marine estuaries, or by natural bio polymers in fresh waters.

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of reaction(s)	Mass Transfer	Engineered	Natural
Disinfection and Sterilization	Enzyme inactivation, protein denaturing or cell lysis	Mass or heat transfer across cell membranes	Destruction or inactivation of pathogens using chemicals, heat irradiations	Destruction or inactivation of organisms by naturally occurring chemical conditions, heat or irradiations (e.g. sunlight)

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of reaction(s)	Mass Transfer	Engineered	Natural
Filtration	Particles or aggregate interception and accumulation at solid surfaces	Microscopic particle transport and interfacial deposition	Removal of SS from water and wastewater by deep bed filtration	Deposition of bacteria and other colloid suspensions in subsurface systems

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of Reaction(s)	Mass Transfer	Engineered	Natural
Ion exchange	Exchange of ions of like but unequal charge at charged surfaces	Interfacial and intra-particle ion diffusion for porous ion exchange resigns	Removal of metals from water and wastewater by ion exchange (e.g. softening demineralization)	Multivalent cation uptake and retardation by soils

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of Reaction(s)	Mass Transfer	Engineered	Natural
Membrane separations	Selective separations of molecular species by microscopic barriers	Molecular diffusion across solid/ water interfaces and within micro porous membranes	Desalination of brakish waters by reverse osmosis and electrodialysis	Separation of dissolved oxygen from water by gill membranes of fish

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of reaction(s)	Mass Transfer	Engineered	Natural
Thermal Transformation	Transformation of chemical species by electron transfer reactions at elevated temperature in heterogeneous phase systems	Gas-solid mass and heat transfer	Incineration of organic matter	Incineration of natural and man made organic material in volcanic eruptions and forest fire

Environmental Systems – Description and Design

Examples of Environmental Processes with Associated Reactions and Mass Transfer Treatment

Process	Nature of reaction(s)	Mass Transfer	Engineered	Natural
Volatilization	Phase transformations by volatilization at moderate (ambient) temperatures	Molecular diffusion across phase interfaces	Stripping of taste and odor causing compounds from drinking waters, ammonia from wastewaters, and volatile organic contaminants from ground waters	Release of hydrogen sulphides from benthic deposits and overlying waters into the atmosphere

Environmental Systems – Description and Design

Processes

Can be divided into two principal categories

- Those affecting the transformation of particular constituents, and
- Those affecting their transport at either the macro-scale (system scale) or the micro-scale (molecular scale)

Transport process at micro-scale:

- Small range diffusion process that occur primarily at the interfaces
- Micro-scale transport from one phase to another is generally referred to as mass transfer
- Micro-scale transport → diffusion of O_2 into the water body
- Such transfer processes often control the rates at which system component contact and subsequently undergo reaction with one another

Macro-scale transport

- Advection: Flow of organic matter from effluent into water bodies
- Diffusion: Eddy diffusion

Environmental Systems – Description and Design

Processes

- It is important to note that the system itself imposes important additional mass transport considerations at the larger scale, i.e. macro-scale mass transport
- Reaction and transport processes, which by themselves might be quiet common in character, thus act in concert in any system to produce changes in composition that are for the most part unique to that system
  - *Each system being like a different symphony (tune) played by the same orchestra*

Environmental Systems – Description and Design

Transformation Processes

- Transformations in environmental systems have their basis in the reactions and interactions of chemical species with one another. All constituents of environmental systems are fundamentally chemicals, thus changes or transformations in them can be described in terms of chemical reactions
  - We must differentiate between transformation processes, and the net changes that occur as a result of such processes in complex systems

Environmental Systems – Description and Design

Transformation Processes

- Transformation processes are controlled by reactions, and in some cases by micro scale mass transfer processes that control the rates of those reactions.
  - Conversely, net changes in systems involve additional (mass transport) considerations that depend more on the systems in which the reactions take place than on the reactions themselves
- Example: Stirred and Unstirred systems
  - Reactions depend on masses (numbers) which are different in different systems

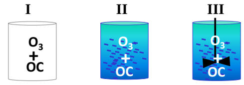
Environmental Systems – Description and Design

Example **Oxidation of Compounds by Ozone**

(An Illustration of the Effects of System Configuration and Physical Characteristics on Process Rates and Efficiencies: Phase and Mixing Effect)

Situation: I II III

Three-One Liter Jars

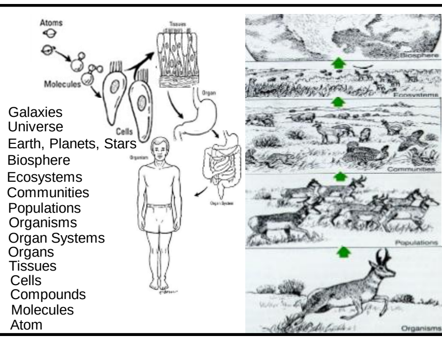


- **Assumptions**
  - **Soluble**
  - **Reaction same in gaseous phase/dissolved state**
  - **Same temperature**

Environmental Systems – Description and Design

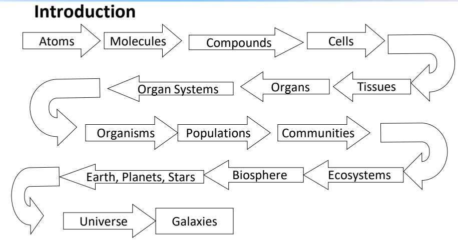
Environment, Systems & Environmental Systems

- Hardware/ Software →Physical/Nonphysical
- Systems → Collection of objects bonded together in some way so that the collection is more than an independent assemblage of parts
- Micro → Macro → Mega Levels (Depending Upon the Boundaries Chosen in a Particular Context)
- Ecosystems → Objects consisting of Living (*Biotic Component*) as well as Non-living (*Abiotic Component*) entities



Environmental Systems – Description and Design

Introduction



Environmental Systems – Description and Design

Environmental Systems .... Some Terms

- **Dynamic System**
  - Continuously undergoes changes
- **Steady Systems**
  - No change
- **Steady State Conditions**
  - No net change observed with time
- **Equilibrium Conditions**
  - Equilibrium laws applicable

Environmental Systems – Description and Design

Environmental Systems .... Processes

- Several processes → Take place simultaneously (in parallel)/one after the other (in series)
- Some can be characterized by Equilibrium Laws, others by rates (kinetics) → Each governed by some basic principles
- Some processes involve living things/occur in living entities (Biological Processes) → Organisms interact with each other and their surroundings →Ecological Process → These occur in systems which have a living component (called the biotic component) and a non-living component (called the abiotic component) → Such systems are referred as Ecosystems.

Environmental Systems – Description and Design

Environmental Systems ……. Processes

- Other processes which do not involve living things but do require some driving mechanism →Physical, Chemical or Physiochemical
- In fact biological processes are nothing but combination of various physical, chemical and physiochemical processes
- But such a combination can not be carried out outside the organism/cell
- Processes → bring changes in the system composition → requires energy or driving force → GOVERNING PRINCIPLE

Environmental Systems – Description and Design

Analysis of Environmental Systems

Environmental Systems ……. Changes

- Change can not take place unless there is a movement → Transport
- Transport → over a long distance or at micro level
- General motion
  - Advection/Eddy Diffusion
  - Takes place in a medium
    - Lithosphere (Solid →Soil)
    - Hydrosphere (Liquid → Water)
    - Atmosphere (Gaseous → Air)
- Constituents having different characteristics
  - Mass Diffusion

Analysis of Environmental Systems

Environmental Systems ……. Changes

- **Transfer from one phase to another → Mass Transfer**
- **Phase Transformation**
  - **Solid ←→ Liquid**
  - **Liquid ←→ Gas**
  - **Gas ←→ Solid**
- **Dynamic (Non-Equilibrium) → Towards (Stable Position) Minimum Energy**
  - **Solid to liquid**
  - **Liquid to gas**
  - **Solid to gas vice versa**

Environmental Systems – Description and Design

Analysis of Environmental Systems

Environmental Systems ……. Changes

- **Transport due to physical/chemical interactions**
- **Physical/ chemical interactions require energy/driving force**
  - body force (attractive) → Gravitational force
  - kinetic energy
  - pressure differences
  - thermal Energy (kT)
  - charge-charge interaction, etc.

Environmental Systems – Description and Design

Analysis of Environmental Systems

- Processes take place in a medium → solid, liquid (water) or gaseous (air)
- May involve
- – One phase, Two Phases, or All Three Phases
- ➢ All these processes involve changes in system composition associated with either input of energy or release of energy
- ➢ Rate and/or extent of change are important
- ➢ All these processes can be imagined to occur in a volume enclosed by some boundaries →Physical/Real or Imaginary → This enclosed volume referred as “Reactor”
- ➢ Natural Process
- – Occurring in nature
- ➢ Engineered Process
- – Artificially Made → Man Made → Anthropogenic

Examples:
- ✓ Settling
- ✓ Coagulation/ Flocculation
- ✓ Adsorption
- ✓ Gas transfer
- ✓ Filtration
- ✓ Precipitation/ Dissolution
- ✓ Oxidation-Reduction
- ✓ Complexation
- ✓ Evaporation
- ✓ Osmosis, etc.

Environmental Systems – Description and Design

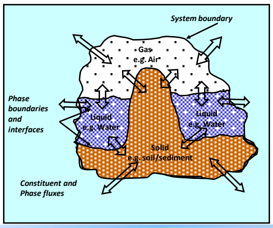
Analysis of Environmental Systems

Analysis Approach

- System Models
- Models → tool to describe or represent an object or a process or a phenomenon
- Ways/Means
  - Physical
  - Mathematical
- Mathematical Models
  - Stochastic
  - Deterministic
- Approaches
  - Theoretical
  - Phenomenological
- Techniques/Tools → Formulation, solution, calibration, verification and simulation
  - Statistical
  - Optimization

Environmental Systems – Description and Design

Analysis of Environmental Systems

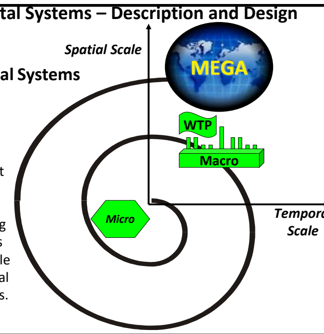


Generalized Multiphase System of Gaseous, Liquid and Solid Phases

It is important to note, however, that the composition of each phase depicted in the figure changes as a result of phase and constituent mass reductions and additions that may occur not only by reactions among constituents within the boundaries of phase, but also by movement of mass across its phase boundaries and accumulations or depletions within interfaces at those phase boundaries.

Environmental Systems – Description and Design

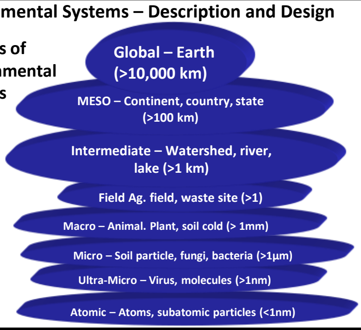
Analysis of Environmental Systems

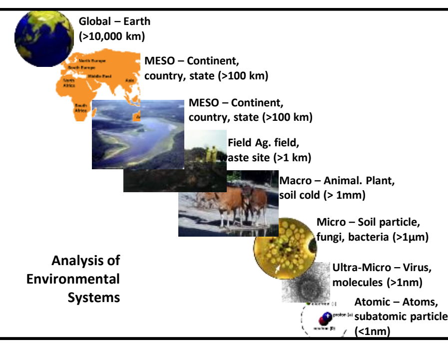


The environment is in fact a continuum of systems involving similar processes over a remarkable range of temporal and spatial scales.

Environmental Systems – Description and Design

Analysis of Environmental Systems

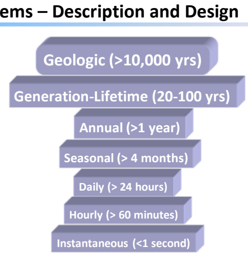




Analysis of Environmental Systems

Environmental Systems – Description and Design

Analysis of Environmental Systems



Environmental Systems – Description and Design

Analysis of Environmental Systems

- All systems are comprised by subsystems; mega-scale systems by macro-scale systems, and macro-scale systems by micro-scale systems. This is why many of the processes discussed earlier can be influenced at the macroscopic scale by similar microscopic mass transfer phenomenon.
- The most fundamental analysis of any system has its origins ultimately at the molecular level and must provide that there is a continuity of principles derived from this scale to the full scale of the system.

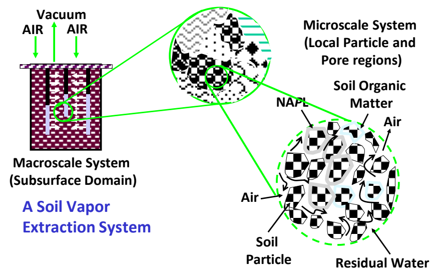
Environmental Systems – Description and Design

Analysis of Environmental Systems

- Any analysis of a process for purpose of description or design must couple descriptions of phenomena at the appropriate micro scale with those of phenomena at the macro scale or mega scales.
- It is essential that we appreciate the role of micro scale process dynamics and understand how to incorporate information on processes at this scale in the characterization, analysis, interpretation, and design of environmental macro scale systems.
- Mass transport, mass transfer and reaction must be separated, understood and described properly

Environmental Systems – Description and Design

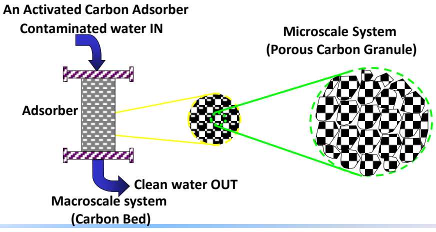
Analysis of Environmental Systems



Environmental Systems – Description and Design

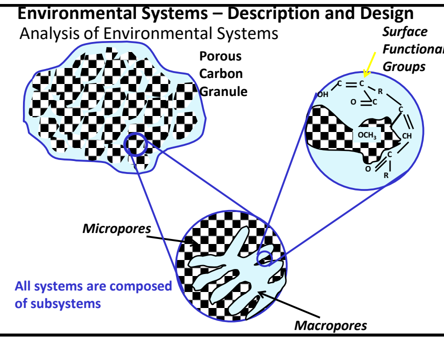
Analysis of Environmental Systems

An Activated Carbon Adsorber



Environmental Systems – Description and Design

Analysis of Environmental Systems



Environmental Systems – Description and Design

Analysis of Environmental Systems

Components and Change

- The components of environmental systems, like the properties of processes and changes that occur within them, are frequently categorized as physical, chemical and biological. In the most elementary sense, however, all of these components are chemical.
- When present in water or wastewater, environmentally reactive components are generally targeted for change, either by removal in phase separation process such as precipitation, adsorption or volatilization, or by transformation in some chemical or biochemical reaction process. The choice of the process depends on certain properties of the targeted compounds, their reactive tendencies, and their resultant susceptibility to specific separation or transformation phenomena.
- The reactor (system) design should be one that maximizes the effectiveness of the process selected.

Environmental Systems – Description and Design

Analysis of Environmental Systems

Measure of Quantity and Concentration

Properties of a system that characterize its inherent mass, energy or momentum, are divided into two: EXTENSIVE and INTENSIVE

- **Extensive Properties & Parameters:** ***Whose magnitude depends on size of the system or sample taken from the system – e.g. mass, volume, heat capacity, calories, etc.***
- **Intensive Properties & Parameters:** ***Conversely, whose magnitude does not depend on the size of the system or sample taken from it – e.g. temperature, pressure, etc.***
- **Expression of Concentration**
  - Mass fraction; Volume fraction; Mole fraction
  - Concentration – moles, equivalents, mg/l

Environmental Systems – Description and Design

Analysis of Environmental Systems

Important Aspect is

- To learn how to quantify information about the important and identifying features of environmental processes and systems, and how to employ descriptive mathematical models to organize that information in ways that allow its use for system analysis, design and performance prediction

Environmental Systems – Description and Design

Analysis of Environmental Systems

Some Basic Concepts of Environmental Systems' Modeling

- The most important properties of a system are its energy, mass and momentum, and its most important dynamics relate to changes in these three fundamental properties
- To understand this is to grasp the most basic tenet of system and process modeling. Each extensive property of a system is fully definable once the boundaries that contain the system are defined
- Moreover, changes in the properties of concern follow well known laws of physics and chemistry, laws that can be written in terms of accurate mathematical expressions
- Our primary focus in terms of extensive system properties is mass, usually the mass of an impurity or contaminant, and the ways and rates of its change in a specific system.
- However, all three extensive systems properties are interrelated, and generally coupled.

Environmental Systems – Description and Design

Analysis of Environmental Systems

System Characterization

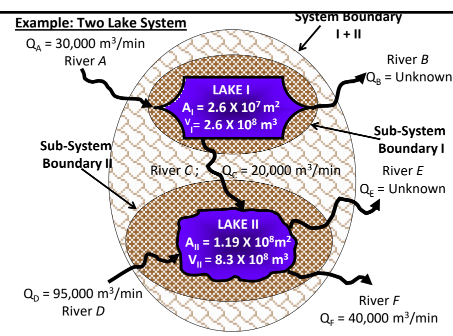
- We will begin to develop rigorous mass and material balance based approached to system characterization and modeling
- These approaches can be extended to analysis and design of systems involving increasingly more complex transport and transformation phenomena
- Before embarking on this, let us first consider a relatively simple environmental system and several sets of different circumstances that lend themselves to intuitive and common sense approach to material balance based "modeling"
- In this we will learn some basic ground rules. Mostly involves *Intution and Common Sense*

Environmental Systems – Description and Design

Analysis of Environmental Systems

Example Two Lake System

- System of two lakes having various inflows and outflows.
- Two of the outflows, Q_B from Lake I and Q_E from Lake II are unknown.
- In this case we are interested in balancing the mass of water, knowing only four flow rates. We assume (given) that respective volumes of the lakes are constant, so there is no net water accumulation in either of them. The first thing to do is to define boundaries.



Environmental Systems – Description and Design

Analysis of Environmental Systems

Objective: Find Q_B and Q_E

Volumes of lakes are constant

i) Define boundary : → system boundary Lake I + Lake II

ii) Mass balance of water

$Q_A + Q_D = Q_B + Q_E + Q_F$ ---- 1

steady state condition → temporarily stable condition

Otherwise

$(Q_A + Q_D) – (Q_B + Q_E + Q_F) = d/dt\,(V_I + V_{II})$ ---- 2

iii) Redefine boundaries:

Lake I – subsystem → $Q_B = Q_A – Q_C = 10{,}000$ m^3/min ---- 3

Lake II – subsystem → $Q_E = Q_C + Q_D – Q_F = 75{,}000$ m^3/min ---- 4

What allows us to write above equation is that mass concentration of water in water is constant and equal to its density ρ_ω

$Q_A\,\rho_\omega – Q_B\,\rho_\omega – Q_c\,\rho_\omega = 0$ ---- 5

Assumption → System involved incurred no change in its properties

Environmental Systems – Description and Design

Analysis of Environmental Systems

- Let us complicate by acknowledging that evaporation may be important/significant (r = 0.5 cm/d → cm³/cm²/d)

- **New sink term**
  → $Q_A \rho_\omega - Q_B \rho_\omega - Q_c \rho_\omega - E_{V,I} \rho_\omega = 0$ ---- 6
  ($E_{V,I} \rho\omega$ = 0.5 / 100 X 1440 m/min X 2.6 X 10^7 m² = 90 m³/min)
  → $Q_C \rho_\omega + Q_D \rho_\omega - Q_E \rho_\omega - Q_F \rho_\omega - E_{V,II} \rho_\omega = 0$
  ($E_{V,II} \rho_\omega$ = 0.5 / 100 X 1440 X 1.19 X 10^8 = 413 m³/min)
  Q_B = 9910 m³/min
  Q_E = 74,600 m³/min

Environmental Systems – Description and Design

Analysis of Environmental Systems

- Constituent mass balance
- Boundary same as before
- Chloride → no transformation → conservative
- Cl is not evaporated
- C_A Cl = 40 mg/l C_D Cl = 60 mg/l
  → Assumption C_B Cl = C_C Cl (complete mixing)

$$C_B Cl = C_C Cl = \frac{30{,}000\ X\ 40}{9{,}910 + 20{,}000} = 40.1 mg/l$$

$$C_E Cl = C_F Cl = \frac{20{,}000\ \ X\ 40.1 + 95{,}000\ \ X\ 60}{74{,}587\ \ - 40{,}000} = 56.7 mg/l$$

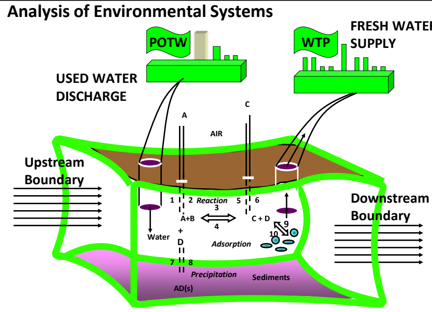
Environmental Systems – Description and Design

Analysis of Environmental Systems

In reviewing the constructs of these intuitive "models", note and contemplate these several important points:

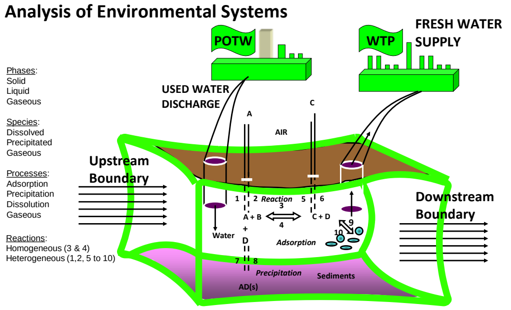
1. Proper selection of boundaries can simplify solutions by reducing the number of unknowns
2. A separate and perhaps somewhat different material balance equation must be written for each component of interest
3. All transport and transformation processes should be first identified in physical context and then translated into equations
4. Any and all assumptions you are making should be identified, stated explicitly and analyzed for merit, and
5. Balanced equations should be developed in terms of general variables first, checked for dimensional consistency, and then quantified with numerical parameter values having appropriate units.

Analysis of Environmental Systems



A Natural Environmental Macroscale System

Analysis of Environmental Systems



A Natural Environmental Macroscale System

Environmental Systems – Description and Design

Process Characterization: Homogeneous Reactions

- Homogeneous reactions are governed by relationships requiring that certain entropy, enthalpy, and energy balances be obeyed among the components or species participating in transformation processes that occur within a single phase. These relationships yield characteristics thermodynamic properties and corresponding equilibrium constants.

$$A + B \Leftrightarrow C + D$$

$$aA + bB \Leftrightarrow cC + dD$$

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K$$

Environmental Systems – Description and Design

Process Characterization: Heterogeneous Reactions

- The chemical relationships governing the hetrogeneous reactions of species are different than those of homogeneous reactions, but they also have their fundamental origins in chemical thermodynamics.
- Henery's law → Characterizes the equilibrium state of phase partitioning for species between dilute aqueous solutions and air/gas phases.
  - P = K_H C → (molar concentration (moles/cum) of substance in the aqueous phase)
  - Concentration in gas phase, expressed in terms of pressure

Environmental Systems – Description and Design

Process Characterization: Heterogeneous Reactions

- Relationships similar to Henry's law exist for the distribution or partitioning of chemical species from water into organic liquids, solids, or biological forms; their precipitation from solution to form solid phases; and their adsorption on to solid surfaces.

Environmental Systems – Description and Design

Process Characterization: Heterogeneous Reactions

Example:

$$[A]^a[B]^b = (K_{sp})_{AB}$$

$$q_e = \frac{Q^0 C}{1 + bc}$$ Langmuir Adsorption Isotherm.

Environmental Systems – Description and Design

Process Characterization: Reaction Rate

- Basis : Law of Mass Action or mass law, which states that rates of reactions are proportional to the masses of the reacting substances

$$r = \frac{dc}{dt} = \oint(\Delta G_r) = \oint(\text{Constitue nts' Mass})$$

- This does not, however, imply that the relative rates of distinctly different reactions can be related to their respective free energies because the coefficients of proportionality may vary from reaction to reaction.

Environmental Systems – Description and Design

Transport Processes:

- A complete description and quantification of compositional changes in a system must account for changes related to transport processes.
- These include :
  - Changes related to the movement of components into or out of the system
  - Distributions of components within its boundaries, and
  - Distribution of components across and within the subsystems comprising the overall system

Environmental Systems – Description and Design

Transport Processes:

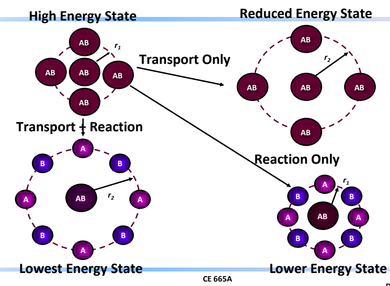
- Elevation, pressure and density differences represent gradient in mechanical energy, while concentration differences represent chemical energy gradients. Similarly, spatial differences in electrical potential (distribution of charges) can cause fluid or solute transport as a result of electrical energy gradient.

Environmental Systems – Description and Design

Intuition and More Common Sense

The bottom line for all transformation and transport processes with which we deal is energy; more specifically the availability of sufficient energy, in the appropriate form, to either make a process happen or to arrest it, whichever of the two is our objective in a given circumstance

Environmental Systems – Description and Design



Environmental Systems – Description and Design

Solid-Liquid-Gas Interactions

- Involve system changes associated with either
  - Input of energy or
  - Release of energy
- Rate and extent of changes are important
- All these interactions can be imagined to occur in space or a volume enclosed by some boundaries (physical / actual or imaginary)
- Such a space or volume is referred as "*Reactor*"

Environmental Systems – Description and Design

Solid-Liquid-Gas Interactions ... ... *Contd*

- What direction, what extent the changes take place?
- Why do the changes take place?
- Governed by certain laws of nature
- Three basic laws of thermodynamics serve as a basis for understanding most of environmental processes/principles

Environmental Systems – Description and Design

Thermodynamics

- Thermodynamics is a study of energy changes accompanying physical and chemical processes
  - Energy changes associated with chemical reactions are of considerable importance
- First it is necessary to review the relationship between heat and work
  - Heat and work are related forms of energy. Heat can be converted into work and work can be converted to heat
- The work in chemical systems usually involves work of expansion either by system or on the system $dw = pdv$

Environmental Systems – Description and Design

Thermodynamics .... continued

- I Law of Thermodynamics
  - Energy can neither be created nor destroyed
  - In chemical systems → energy involved is most easily handled in terms of three quantities
    - The work (w)
    - The heat (q)
    - Energy stored in the system

Environmental Systems – Description and Design

Thermodynamics ....continued

$$\Delta E = q - w \qquad \begin{aligned} \Delta E &= \text{Internal Energy} \\ q &= \text{Heat Flow} \\ w &= \text{Work Done by the System} \end{aligned}$$

$$q = +\text{ve (if heat absorbed); } -\text{ve (if heat released)}$$

$$w = +\text{ve work done by system,}$$

$$-\text{ve work done on system or done by surrounding}$$

$$\Delta E = q_v$$

- Although this is convenient for constant-volume systems, most chemical systems of interest to environmental engineers are open to the atmosphere and so operate under constant pressure rather than constant volume. For such systems, the concept of enthalpy has been developed.

Environmental Systems – Description and Design

Thermodynamics ....continued

Enthalpy

$$H = E + pv$$

$$\begin{aligned} \Delta E &= E_2 - E_1 = q_p - w \\ &= q_p - p(v_2 - v_1) \\ \text{or } & (E_2 + Pv_2) - (E_1 + Pv_1) = q_p \\ \text{or } & H_2 - H_1 = q_p \\ \Delta H &= q_p \text{ (Heat absorbed at constant T \& P)} \end{aligned}$$

Change in Enthalpy $\rightarrow \Delta H \rightarrow +\text{ve} \rightarrow$ Endothermic Reactions; $\Delta H \rightarrow -\text{ve} \rightarrow$ Exothermic Reactions

H is difficult to measure, we are normally interested, however, in the change in enthalpy.

Standard State → 25°C & 1 atm

ΔH^{o}_{298} = -68.230 kcal → H_2 (g) + ½ O_2 (g) → H_2O

Environmental Systems – Description and Design

Thermodynamics ....continued

Entropy:

- We are concerned, in one way or another, with the state of equilibrium and the tendency of system to move spontaneously. The concept of *entropy* was developed from the search for a thermodynamic function that would serve as a general criterion of spontaneity of physical and chemical changes.
- The concept of entropy is based on II Law of Thermodynamics, which in essence states that all systems tend to approach a sate of equilibrium.

Environmental Systems – Description and Design

- Work can be obtained only when the system is not in equilibrium. At equilibrium → No process tends to occur spontaneously, and no chemical or physical changes are brought about.

$$ds = \frac{dq_{rev}}{T}$$

$$\Delta s = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T}$$

- q_{rev} → heat absorbed in a chemical change i.e. infinitely slow and reversible.
- Entropy of a system at 0 K is ZERO (II[nd] Law of Thermodynamics)

Environmental Systems – Description and Design

Thermodynamics ....continued

Significance of Entropy

- When a spontaneous change occurs in a system, it will always be found that the total entropy change for everything involved is positive. → Thus all spontaneous changes in an isolated system occur with an increase of entropy.
- On the molecular scale, entropy has a statistical basis.
- The more highly probable or random a system becomes, the higher will be its entropy.
- Example: Two inert gases in a closed container → become randomly mixed without a change in internal energy, but with increased entropy.

Environmental Systems – Description and Design

Thermodynamics ....continued

Free energy

- Both energy and entropy factors must be considered in order to determine what process will occur spontaneously

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \text{(T \& P Const)}$$

$$= q_{rev} - w_{max} + p\Delta v - q_{rev}$$

$$\text{and } -\Delta G = w_{max} - p\Delta v \quad (p\Delta v \rightarrow \text{work wasted in expanding the system})$$

$$= w_{useful}$$

$$\begin{aligned} \Delta H &= H_2 - H_1 \\ &= \Delta E + p\Delta v \\ &= q - w + p\Delta v \end{aligned}$$

if process is slow, no losses,

$$q = q_{rev}$$

Environmental Systems – Description and Design

Thermodynamics **…………continued**

- In principle, any process that tends to proceed spontaneously can be made to do useful work. Since the free energy change measures the useful work that might be obtained from a constant – pressure process, it is a measure of a spontaneity of the process.
- Consider the change from a to b in a constant pressure system.

a ⇌ b

a → b if ΔG is negative

a ← b if ΔG is positive

if ΔG = 0 (process can not proceed; the system is in equilibrium)

Environmental Systems – Description and Design

Thermodynamics **…………continued**

- This is particularly significant relationship, and for the chemist it is one of the most important in thermodynamics.
- In order for the concept of free energy to be useful, a reference point for determining free energy changes must be available.
- As in case of enthalpy, reference point (condition) is taken as 25ºC and 1 atm pressure; and zero value is assigned to free energy of stable form of elements at this point.

Environmental Systems – Description and Design

Thermodynamics **…………continued**

- In addition, the hydrogen ion at unit activity (=1 N solution) is assigned a standard free energy of zero.
- The standard free energy of a compound (ΔG^o_{298}) is the free energy of formation of that compound from its elements, considering reactants and products all to be in the standard state at 25ºC and 1 atm.

Environmental Systems – Description and Design

Thermodynamics **…………continued**

- Free energies can also be used to determine the equilibrium state to which the reaction carries the system, as well as the direction.
- The direction of reaction is dependent upon the concentration of reactants and products, and so this must be considered in free energy calculations.

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta G = \Delta G^0 + RT \ \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

ΔG	→	reaction free energy changes, *cal*
R	→	1.99 cal/deg-mol
ΔG^0	→	standard free energy changes, *cal*
T	→	absolute temperature, K

- Comparison of Reaction Quotient $Q = \{(C)^c (D)^d / (A)^a (B)^b\}$ with K

Environmental Systems – Description and Design

Thermodynamics **…………continued**

At equilibrium, no further driving force is operative, i.e. ΔG = 0 and thus

$$\Delta G^0 = -RT \ \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

ΔG^0 = -RT ln K or -ln K = ΔG^0/RT = pK

Free Energy of Formation

$$\Delta G = G_{final} - G_{initial}$$

Under Standard Conditions

$$\Delta G^o_{reaction} = \sum \Delta G^o_{\substack{\text{formation} \\ \text{of products}}} - \sum \Delta G^o_{\substack{\text{formation} \\ \text{of reactants}}}$$

Environmental Systems – Description and Design

Thermodynamics **…………continued**

Example

$$Fe^{+2}_{(aq)} + 2HCO^-_{3(aq)} + Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons Fe(OH)_{3(s)} + 2CO_{2(g)} + 2Cl^- + H^+_{(aq)}$$

$$\Delta G^0_{reaction} = \{-166.0 + 2(-94.25) + 2(-31.35) + 0\} - \{-20.30 + 2(-140.31) + 0 + (-56.69)\} = -59.59 \text{ kcal}$$

Chemical Species	Free Energy of Formation, kcal/mole
Fe^{+2} (aq)	- 20.30
HCO_3^- (aq)	- 140.31
Cl_2 (g)	0
H_2O (l)	- 56.69
$Fe(OH)_3$ (s)	- 166.0
CO_2 (g)	- 94.25
Cl^- (aq)	- 31.35
H^+ (aq)	0 (by convention)

Environmental Systems – Description and Design

Thermodynamics …………continued

Enthalpy of Formation

$\Delta H^o_{reaction}$ calculated in the same way as $\Delta G^o_{reaction}$.

Chemical elements in the standard state (P = 1 atm; T = 298 K) are assigned a value of zero enthalpy of formation.

All compounds are assigned a Standard Molar Enthalpy of Formation i.e $\Delta H^o_{\text{formation}}$.

$$\Delta H^o_{reaction} = \sum \Delta H^o_{\substack{\text{formation of}\\ \text{products}}} - \sum \Delta H^o_{\substack{\text{formation of}\\ \text{reactants}}}$$

Environmental Systems – Description and Design

Thermodynamics …………continued

Notations:

- H_2 (g) + ½ O_2 (g) → H_2O (lq)
- Δ H^0_{298} = - 68.320 kcal
- Symbols in parenthesis after each element or compound indicate standard state of the elements or compounds
- Superscript zero on the enthalpy indicates a standard heat of formation with reactants and products at 1 atm
- The absolute temperature is written as subscript.

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles

- Chemical Equations – Expression of what happens during a chemical change
- E.g. $FeCl_3$ + 3NaOH → $Fe(OH)_3$ + 3NaCl
- Unbalanced / Balanced → Atoms do not disappear/ are not produced during a chemical change

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles

How to balance a chemical equation

- Correct formulae for reactants/products
- Reactants to left and product to right
- Balance all atoms, one by one, H and O at the end
- Final balanced equation should contain whole number coefficients in the smallest ratio possible e.g.

4HgO → 4Hg + $2O_2$ (incorrect)
2HgO → 2 Hg + O_2 (correct form)

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ……. *Contd.*

Notations

$\longrightarrow$	Yields
$\rightleftarrows$	Reversible
↑ or (g)	Gas e.g. CO_2 (g) or CO_2↑
↓ or (s)	Solid / Precipitate e.g. $CaCO_3$ (s) or $CaCO_3$↓
(aq)	Aqueous solutions/substance dissolved in water e.g. [Ca^{+2}(aq)]
(l)	Liquid (written after substance)

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ……. *Contd.*

Heat in chemical reactions

- Energy absorption/heat absorption
  - Endothermic
- Energy release/heat release
  - Exothermic

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ***……. Contd.***

Types of Chemical Reactions

- Chemical reactions without change in oxidation state of elements → Mathematical Reactions
  - Occurs because one or more of the product is shifted away from the field of the reaction

E.g. :

1. Liberation of gas
   $CO_3^{-2}\ (aq) + 2H^+\ (aq) \rightarrow CO_2\ (g) + H_2O\ (l)$
2. Precipitation
   $Ca^{+2}\ (aq) + CO_3^{-2}\ (aq) \rightarrow CaCO_3\ (s)$
3. Formation of Slightly Ionized Substance
   $CN^-(aq) + H_2O\ (l) \rightarrow OH^-(aq) + HCN\ (aq)$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ***……. Contd.***

Oxidation – Reduction (REDOX) Reactions

OXIDATION:

- Oxidation is the loss of electron/donation of electron
- Electron looser/Electron donor
- Results in increase in the oxidation number
- Reducer or one which gets oxidized

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ***……. Contd.***

Oxidation – Reduction (REDOX) Reactions

REDUCTION:

- Reduction is the gain of electron/acceptance of electron
- Electron gainer/ Electron acceptor
- Oxidizer or one which gets reduced
- Results in decrease in oxidation number

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ***……. Contd.***

Example

$$\overset{0}{Cl_2} + \overset{+2}{Mn}(aq) + 2\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow \overset{+4}{Mn}\overset{-2}{O_2}(s) + 2\overset{-1}{Cl^-}(aq) + 4\overset{+1}{H^+}(aq)$$

Increase in Oxidation Number

Loss of 2 electrons /Mn atoms

Decrease in Oxidation Number

Gain of 1 electron/ Cl atom

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ***……. Contd.***

- In a balanced equation, number of electrons lost in the oxidation process must be equal to the number of electrons gained in the reduction process

$$4\overset{+1}{K_2}\overset{+6}{Cr_2}\overset{-2}{O_7} + \overset{0}{C_6}\overset{+1}{H_{12}}\overset{-2}{O_6} + 32\overset{+1}{H} \rightarrow 8\overset{3+}{Cr} + 6\overset{+4}{C}\overset{-2}{O_2} + 22\overset{+1}{H_2}\overset{-2}{O} + \overset{+1}{K}^+$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ***……. Contd.***

Balancing O-R Reaction (through example)

$$NO_3^-(aq) + SO_3^{-2}(aq) \rightarrow N_2(g) + SO_4^{-2}(aq)$$

Assign oxidation numbers

$$\overset{+5}{N}\overset{-2}{O_3} + \overset{+4}{S}\overset{-2}{O_3} \rightarrow \overset{0}{N_2} + \overset{+6}{S}\overset{-2}{O_4}$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles .... *Contd.*

Separate Oxidation & Reduction into two half reactions

Oxidations

$$SO_3^{-2} \rightarrow SO_4^{-2}$$

Reduction

$$NO_3^{-} \rightarrow N_2(g)$$

Balance all atoms with exception of O and H

$$SO_3 \rightarrow SO_4$$
$$2NO_3 \rightarrow N_2$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles .... *Contd.*

To each half reactions, add number of electrons

$$SO_3^{-2} \rightarrow SO_4^{-2} + 2e^-$$
$$10e^- + 2NO_3^{-1} \rightarrow N_2$$

Balance Charge of each reaction with H- or OH- ions

$$SO_3^{-2} + 2H^+ \rightarrow SO_4^{-2} + 2e^- + 4H^+$$
$$10e^- + 2NO_3^- + 12H^+ \rightarrow N_2$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles .... *Contd.*

Balance H & O atoms using H_2O

$$SO_3^{-2} + 2H^+ + H_2O \rightarrow SO_4^{-2} + 2e^- + 4H^+$$
$$10e^- + 2NO_3^- + 12H^+ \rightarrow N_2 + 6H_2O$$

Make number of electrons same in both half reactions

$$5SO_3^{-2} + 10H^+ + 5H_2O \rightarrow 5SO_4^{-2} + 10e^- + 20H^+$$
$$10e^- + 2NO_3^- + 12H^+ \rightarrow N_2 + 6H_2O$$

Add the two half reactions

$$2NO_3^- + 5SO_3^{-2} + 2H^+ \rightarrow N_2 + 5SO_4 + H_2O$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles .... *Contd.*

Definitions

- **Solutions**
  - Indicate a system in which one or more substances are uniformly and homogenously dissolved or blended into another substance

There are two components in a solution

- Solute – the substance that is dissolved
- Solvent – the substance which does dissolving and which is present in the greatest quantity

Physicochemical Principles - Fundamentals

Chemical Reactions : Basic Principles .... *Contd.*

- Three states of matter:
  - Solid
  - Liquid
  - Gas
- Nine different types of solution
- The most important in water industry is *Solids in Liquid*

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles .... *Contd.*

- Concentration of solutions → Physical and chemical units
- Solubility → Temperature dependent
- Saturated solution:
  - Solute (undissolved) ←→ Solute (dissolved)
  - Rate of dissolution = Rate of crystallization
- Unsaturated solution

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ……. *Contd.*

Physical

(a) Weight – percent solution

$$= \frac{\text{g solute}}{\text{g solute} + \text{g solvent}} \text{ X } 100$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ……. *Contd.*

Chemical

- **Molarity or molar solution**
  1g MW per liter of solution

$$M = \frac{\text{g solute}}{(\text{g Mol Wt})(\text{liters of solution})}$$

- **Normality or normal solution**
  1 g Equivalent Wt per liter of solution

$$N = \frac{\text{g solute}}{(\text{g Eq Wt of solute})(\text{liters of solution})}$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ……. *Contd.*

Important

- The number of chemical equivalents in a given amount of substance is defined only in terms of specific reactions involving that substance
- The term Equivalent Weight is defined as number of grams of substance that will provide Avogadro's Number (A_n) of units of reaction (e.g. A_n number of protons transferred, A_n number of electrons transferred;

$$\text{g Eq Wt} = \frac{\text{g Mol Wt}}{C_C}$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ……. *Contd.*

- C_C → combining capacity of the solute, depends on the reaction for which it is used. To determine C_C, the following assumptions are generally made
  - Acids: C_C = number of available protons, where n represents this number in the chemical formula H_nA
  - Bases: C_C = number of available hydroxyls, where n represents this number in the chemical formula $B(OH)_n$
  - Salts: total number of positive or negative charges per formula
  - Oxidizing or Reducing agents: C_C = number of electrons transferred per formula
- e.g.

$$Cr_2O_7^{-2} + 2Pb^{+2} + H_2O \rightarrow 2PbCrO_4 + 2H$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ……. *Contd.*

- Identify type of reaction → Mathematical/O-R
- Compute number of positive charges/negative charges

$$Cr_2O_7^{-2} + 2Pb^{+2} + H_2O \rightarrow 2PbCrO_4 + 2H$$

$$\text{g Eq Wt} = \frac{\text{g MW}}{2} = \frac{294.2}{2} = 147.1$$

$$Cr_2O_7^{-2} + 14H + 6e \rightarrow 2Cr^{+3} + 7H_2O$$

$$g \text{ Eq Wt} = \frac{294.2}{3} = 98.1$$

$$\text{mg/l as } CaCO_3 = [\text{mg/l of substance}]\left[\frac{\text{Eq Wt of } CaCO_3}{\text{Eq Wt of substance}}\right]$$

Environmental Systems – Description and Design

Chemical Reactions : Basic Principles ……. *Contd.*

The Dilution Equation

$$M_1v_1 = M_2v_2$$

$$c_1v_1 = c_2v_2$$

Environmental Systems – Description and Design

Process Kinetics

- Understanding chemical process reactions require knowledge of:
  1. Relative equilibrium position of reaction → obtained from chemical thermodynamics.
  2. Rate at which reaction equilibrium is approached →obtained from Chemical Kinetics

Reaction Rates : $\frac{-dCr}{dt} or \frac{dCp}{dt}$

$NH_4^+ + 1.5\ O_2 \rightleftharpoons NO_3 + 4H^+$

Environmental Systems – Description and Design

Chemical Kinetics …….. continued

- Relative rate of change for each species is defined by the molar coefficient in the balanced chemical equation
  - The specific numerical value for the rate depends on species considered
  - The overall rate is defined as the rate of change in concentration divided by molar coefficient in balanced equation

$$-\frac{dC_{NH_4}/dt}{1} \quad -\frac{dC_{O_2}/dt}{1.5} \quad +\frac{dC_{NO_3}/dt}{1} \quad +\frac{dC_H/dt}{4}$$

- Most of the kinetic data are analyzed on the basis of the rate of change for a particular chemical species and not in terms of the rate for the overall chemical change

Environmental Systems – Description and Design

Chemical Kinetics …….. continued

Rate and Order

- Chemical reaction may be classified
  - On the basis of stoichiometry
  - On a kinetic basis → useful in defining the kinetics
- Classification on the basis of order is generally applicable for
  - Essentially irreversible reactions
  - Initial stages of reversible reactions
  - Reversible reactions, whose position of equilibrium lies far to the right

Environmental Systems – Description and Design

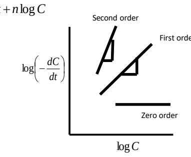
Chemical Kinetics …….. continued

Reaction Order

$$-\frac{dC}{dt} = kC^n$$

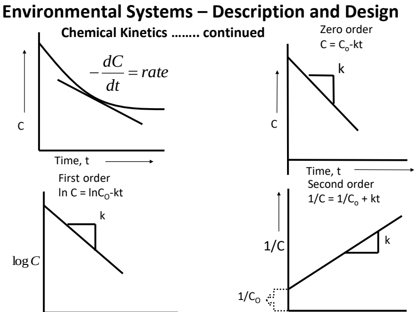
$$\log\left(-\frac{dC}{dt}\right) = \log k + n \log C$$

- Zero order → $\frac{dC}{dt} = -k$
- First order → $\frac{dC}{dt} = -kC$
- Second order → $\frac{dC}{dt} = -kC^2$
- n^{th} order, etc



Environmental Systems – Description and Design

Chemical Kinetics …….. continued



Environmental Systems – Description and Design

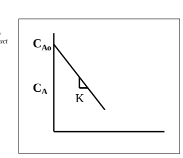
Various Types of Reactions

- <u>**Zero order reaction**</u>
  - **Rate of reaction is independent of the concentration of the reactant**

$$\underset{Reactant}{A} \xrightarrow{k} \underset{Product}{B}$$

$$\frac{d[C_A]}{dt} = -K[C_A] = K$$

$$C_A = C_{Ao} - Kt$$



Environmental Systems – Description and Design

Various Types of Reactions

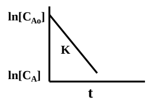
- **<u>First order reaction</u> → rate of reaction is directly proportional to the concentration of the reactant.**

$$\underset{Reactant}{A} \xrightarrow{K} \underset{Product}{B}$$

$$\frac{\partial [CA]}{\partial t} = K[CA]$$

Or

$$\ln[C_A] = \ln[C_{Ao}] - Kt$$



Example:
(1) BOD exertion
(2) Chick's law of disinfection
(Most commonly used /applicable rate of reaction in environmental engineering)

Environmental Systems – Description and Design

Various Types of Reactions

3. <u>Second order reaction</u> → rate of reaction is proportional to the second power of concentration of reactant.

$$A \xrightarrow{K} B$$

$$\frac{d[C_A]}{dt} = -KC_A^2$$

$$\frac{1}{C_A} - \frac{1}{C_{A_0}} = Kt$$

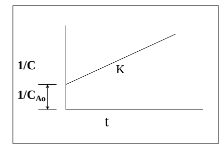
Microbial growth

$$S + X \rightarrow CO_2 + H_2O + More X$$

$$\frac{dS}{dt} = K_1[S][X]$$

$$\frac{dCO_2}{dt} = K_2[S][X] \quad \text{for } CO_2$$

$$\frac{dX}{dt} = K_3[S][X]$$



Environmental Systems – Description and Design

Various Types of Reactions

4. **<u>Consecutive reaction</u> →**

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

Decay of Radioactive Elements

$$\underset{\text{One Radioactive element}}{N_1} \xrightarrow{K_1} \underset{\text{Another Radioactive element}}{N_2} \xrightarrow{K_2} \underset{\text{Stable product}}{N_3}$$

2. Oxidation of Ammonia to NO_2 to NO_3 by nitrifying organisms

$$NH_3 \xrightarrow[k_1]{O_2} N_2 \xrightarrow[K_2]{O_2} N_3 \ \text{(stable)}$$

Environmental Systems – Description and Design

Various Types of Reactions

Let us consider,

$$N_1 \xrightarrow{K_1} N_2 \xrightarrow{K_2} N_3$$

Also, N_2 is decomposing to N_3 at

$$-\frac{dN_1}{dt} = k_1 N_1 = rate\ of\ decomposition$$

$$= \frac{dN_2}{dt} = rate\ of\ formation\ of\ N_2 \qquad \frac{dN_2}{dt} = -k_2 N_2$$

$$\frac{dN_1}{dt} = -K_1 N_1$$

$$\Rightarrow N_1 = N_1^0 e^{-K_1 t}$$

$$\frac{dN_2}{dt} = K_1 N_1 - K_2 N_2$$

$$or - \frac{dN_2}{dt} = K_2 N_2 - K_1 N_1^0 e^{-K_1 t} \ (1)$$

Environmental Systems – Description and Design

Various Types of Reactions

For this linear equation of first order (first order linear differential equation), assume a solution of the form,

$$N_2 = uv$$

Where, u and v are function of time t.

$$-\frac{dN_2}{dt} = K_2 N_2 - K_1 N_1^0 e^{-K_1 t} \ (1)$$

$$\frac{\partial N_2}{\partial t} = u\frac{\partial v}{\partial t} + v\frac{\partial u}{\partial t}$$

$$u\frac{\partial v}{\partial t} + v\frac{\partial u}{\partial t} + K_2 N_2 - K_1 N_1^0 e^{-K_1 t} = 0$$

$$u\frac{\partial v}{\partial t} + v\frac{\partial u}{\partial t} + K_2 uv - K_1 N_1^0 e^{-K_1 t} = 0$$

$$or, \ u\left(\frac{\partial v}{\partial t} + K_2 v\right) + v\frac{\partial u}{\partial t} - K_1 N_1^0 e^{-K_1 t}$$

Choosing v such that $\frac{\partial v}{\partial t} + K_2 v = 0$

$$\frac{\partial v}{\partial t} = -K_2 v$$

$$\int \frac{\partial v}{v} = -K_2 \int \partial t + C$$

$$\ln v = -K_2 t + c$$

$$\text{OR} \ \ v = e^{-kt+c} \ = \ c, e^{K_2 t}$$

Environmental Systems – Description and Design

Various Types of Reactions

Substituting value of v, we get

$$c_1 e^{-K_2 t}\frac{du}{dt} - K_1 N_1^0 e^{-K_1 t} = 0$$

$$or, \frac{du}{dt} = \frac{K_1 N_1^0}{c_1}\frac{e^{-K_1 t}}{e^{-K_2 t}}$$

$$or, \frac{\partial u}{\partial t} = \frac{K_1 N_1^0}{c_1} e^{(K_2 - K_1)t}$$

$$or, u = \frac{K_1 N_1^0}{c_1(K_2 - K_1)} e^{(K_2 - K_1)t} + \text{constant}$$

$$N_2 = uv = \frac{K_1 N_1^0}{c_1(K_2 - K_1)} e^{(k_2 - k_1)t} c_1 e^{-k_2 t} + \text{constant } c_1 e^{-k_2 t};$$

Environmental Systems – Description and Design

Various Types of Reactions

Boundary condition at t = 0 $N_2 = N_2^0$

$$\Rightarrow c = N_2^0 - \frac{K_1 N_1^0}{K_2 - K_1}$$

$$\therefore N_2 = \underbrace{\frac{K_1}{K_2 - K_1} N_1^0 \left[e^{-K_1 t} - e^{-K_2 t}\right]}_{\text{(Formation of } NO_2 \text{ and conversion of } NO_2 \text{ to } NO_3\text{)}} + \underbrace{N_2^0 e^{-K_2 t}}_{\text{(Conversion of } NO_2 \text{ initially present to } NO_3\text{)}}$$

For concentration of N_3, we can write

$$\frac{\partial N_3}{\partial t} = K_2 N_2 = \frac{K_2 K_1 N_1^0}{K_2 - K_1}\left[e^{-K_1 t} - e^{-K_2 t}\right] + K_2 N_2^0 e^{-K_2 t}$$

$$N_3 = \underbrace{\frac{N_1^0}{K_2 - K_1}\left[K_1 e^{-K_2 t} - K_2 e^{-K_1 t}\right]}_{from\ N_1^0} + \underbrace{N_2^0\left[1 - e^{-K_2 t}\right]}_{from\ N_2^0} + \underbrace{N_3^0}_{Initial}$$

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Environmental Systems – Description and Design

Various Types of Reactions

Similar Differential Equation (Streeter-Phelps Equation) can be derived for DO deficit in streams

$$\frac{\partial D}{\partial t} = K_1 L - K_2 D \Rightarrow \frac{K_1 L_a}{K_2 - K_1}\left[e^{-K_1 t} - e^{-K_2 t}\right] + \underbrace{D_a e^{-K_2 t}}_{\text{(initial DO deficit)}}$$

Reversible Reactions

$$A \underset{k_2}{\overset{k_1}{\leftrightarrow}} B$$

$$\frac{\partial C_A}{\partial t} = -K_1[C_A] + K_2[C_B]$$

First order reversible reaction used in adsorption/ion exchange, etc.
(Basis for Langmuir Adsorption Isotherm equation)

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Environmental Systems – Description and Design

Various Types of Reactions

Complex Reactions

$$A \xleftrightarrow{K_1} I \xrightarrow{K_2} B$$

The net rate of change of I

$$\frac{\partial C_I}{\partial t} = K_1[C_A] - \{K_{-1}(C_I) + K_2(C_I)\}$$

for maximum production of B, there should be no accumulation of I

$$i.e. \frac{\partial C_I}{\partial t} = 0 \Rightarrow K_1[C_A] = (K_{-1} + K_2)C_I$$

A typical example of this type of reaction is <u>Enzyme Substrate Complex Reaction</u>

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Environmental Systems – Description and Design

Various Types of Reactions

Complex Reaction: Enzyme-Substrate Reaction

$$\underbrace{E + S \underset{k_2}{\overset{k_1}{\Longleftrightarrow}} ES}_{\text{Reversible combination of E \& S to form ES Complex}} \underbrace{\overset{k_3}{\Longrightarrow} E + P}_{\text{Irreversible decomposition of ES to E \& P}}$$

When the concentration of ES complex appears constant a dynamic equilibrium (steady state) condition prevails, where

Rate of complex formation = rate of complex decomposition

$$k_1[E][S] = k_2[ES] + k_3[ES]$$

$$or \frac{[E][S]}{[ES]} = \frac{k_2 + k_3}{k_1} = k_m \rightarrow \text{Michaelis constant}$$

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Environmental Systems – Description and Design

Various Types of Reactions

The maximum reaction rate for formation of product will occur when all E is associated with ES i.e. $R_{max} = K_3 [E_{TOTAL}]$

At any other stage , $R = K_3 [ES]$

Also, $$[E_{total}] = [E] + [ES]$$

$$or, [E] = \frac{R_{max}}{k_3} - \frac{R}{k_3}$$

Substituting for "E" from (1), we get

$$\frac{k_m[ES]}{[S]} = \frac{R_{max}}{k_3} - \frac{R}{k_3}$$

$$or, [S]\,[R_{max} - R] = k_m k_3 [ES] = k_m R$$

$$\therefore R = \frac{R_{max}[S]}{k_m + [S]} \quad \text{Michaelis - Menten Equation}$$

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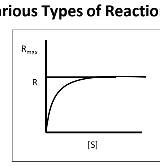
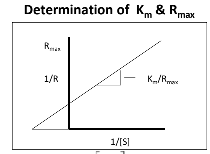
Environmental Systems – Description and Design

Various Types of Reactions

Determination of K_m & R_{max}





$$\frac{1}{R} = \left[\frac{k_m}{R_{max}}\right]\frac{1}{S} + \frac{1}{R_{max}}$$

Line Weaver - Brake Plot

Segel (1968) Cited in Benfield & Randall (1980)
Zero order S $\geq$ 100 K_m
First order S $\leq$ 0.01 K_m
For all practical purposes S $\leq$ K_m first order may be assumed
Goldman *et al* for all practical purposes S $\leq$ k_m

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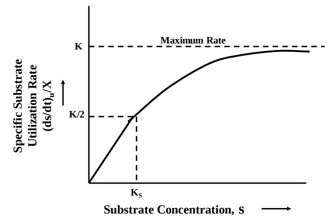
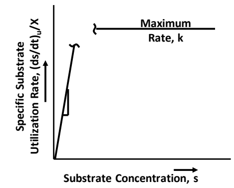
Various Types of Reactions



Environmental Systems – Description and Design

Various Types of Reactions



Relationship Between Substrate Utilization Rate and Substrate Concentration

Environmental Systems – Description and Design

Various Types of Reactions

Kinetics: Microbial Growth and Substrate Utilization

$$R = \frac{R_{\max}[S]}{k_m + [S]} \quad \text{Michaelis - Menten Equation}$$

$$\mu = \frac{\mu_{\max}[S]}{k_s + [S]} \quad \text{Monod's Equation}$$

$$q = \frac{q_{\max}[S]}{k_s + [S]}$$

$$q = q_m \text{ for } S \gg k_s$$

$$q = [q_{\max} / k_s]S = kS$$

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Chemical Kinetics …….. continued

Reaction Order

- Sum of the exponents on the concentration of the reactants in the differential rate law

$$\frac{dC_A}{dt} = -KC_A(C_B)^2 \rightarrow$$

Third order reaction on the basis of individual components, first order with respect to A and second order with respect to B

Environmental Systems – Description and Design

Chemical Kinetics …….. continued

Pseudo First Order

$$-\frac{dC_A}{dt} = KC_AC_B \rightarrow very\ high$$

Rate, Order and Stoichiometry

$$aA + bB \rightleftharpoons cC + dD$$

$$(K_C)_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Environmental Systems – Description and Design

Chemical Kinetics …….. continued

Equilibrium Independent of Pathway

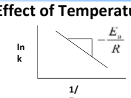
- Order of a chemical reaction can not be predicted from stoichiometry
- Exponents in differential rate law not same as stoichiometric coefficients
- n can only be determined by experimentally

$$A + B \rightarrow P$$

$$-\frac{dC_A}{dt} = kC_A(C_B)^O = -kC_A \qquad -\frac{dC_A}{dt} = kC_AC_B$$

Environmental Systems – Description and Design

Effect of Temperature on Rate Constant (Arrhenius Equation)



$$\ln\frac{k_2}{k_1} = Const.(T_2 - T_1)$$

$$or\ \frac{k_2}{k_1} = e^{const(T_2 - T_1)}$$

$$= \Theta^{(T_2 - T_1)}$$

$$\frac{\partial(\ln k)}{\partial T} = \frac{E_a}{R}\frac{1}{T^2}$$

$$or\ \ln k = -\frac{E_a}{R}\frac{1}{T} + \ln B\ (\text{constant})$$

Integrating between the two temperature limits (T_1 & T_2)

$$\ln\frac{k_1}{k_2} = \frac{Ea(T_2 - T_1)}{RT_1T_2}$$

E_a → For biological WWT Process generally will fall within the range 2000-20,000 cal/mole or 8400-8,4000 J/mole
R → 8.314 J/mole/°K

Assumptions:
1) volumetric flow rate constant
2) no evaporation (isothermal)
3) reaction occurring within the boundaries
4) complete mixing
5) reaction order

Environmental Systems – Description and Design

Chemical Kinetics …….. continued **Catalysis**

- ΔG indicate spontaneity of the reaction
- Rate of certain spontaneous reaction is very low
  - May take years to detect change in concentration
- Before molecules react, they must pass through a configuration, known as transition state or activated complex
  - Which has energy content greater than the reactants or product
  - Added energy is required → free energy of activation
  - Inversely related to rate of reaction
  - Kinetics depend upon stoiciometry of transition state and not reactant
  - However, in most cases concentration of activated complex is a function of reactant concentration.

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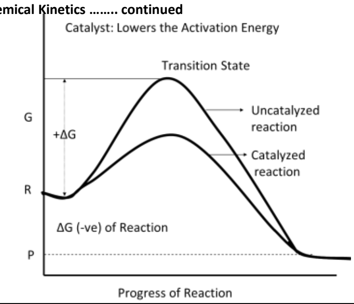
Chemical Kinetics …….. continued **Catalysis**



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Chemical Kinetics …….. continued **Catalysis**

Catalysis by H ions

$$A + nH^+ \rightarrow P + nH^+$$

$$-\frac{dC_A}{dt} = K_H[H^+]^n C_A = K_{obs}C_A$$

Catalysis by OH ions

$$A + nOH^- \rightarrow P + n(OH)$$

$$-\frac{dC_A}{dt} = K_{OH}[OH^-]^n C_A = K_{obs}C_A$$

Environmental Systems – Description and Design

Chemical Kinetics …….. continued **Catalysis**

Autocatalysis

$$A + P \rightarrow P + P$$

$$-\frac{dC_A}{dt} = KC_AC_P$$

Environmental Systems – Description and Design

Reproduction and Growth of Microorganisms

- Growth of a Bacterial Culture

  1 → 2 → 4 → 8 → 16 → 32 → …………

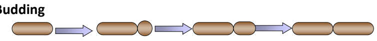
  - This increase may be expressed as a geometric progression in the following manner:

    $1 \rightarrow 2^2 \rightarrow 2^3 \rightarrow 2^4 \rightarrow 2^5 \rightarrow \ldots\ldots 2^n$
  - Where the exponent *"n"* refers to the number of generations.
  - Generation Time:
    - The time interval required for each microbe to divide, or for the population in a culture to double, is known as generation time.
    - Not all species of microorganisms have the same generation time. For *Escherichia Coli,* the generation time in a rich medium may be as short as 12.5 min.
    - For *Mycobacterium tuberculosis,* it is 13 to 15 h.
    - However, the population doubling time is not same for a particular species of microorganism under all conditions.
    - *Escherichia Coli,* for example, will take much longer to double its population or may not even double in a nutritionally poor medium.
    - Population doubling times are strongly influenced not only by the nutritional composition of the medium, but also by the physical conditions of incubation.

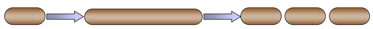
Environmental Systems – Description and Design

Cell reproduction by unicellular procaryotes other than by transverse binary fission:

Budding



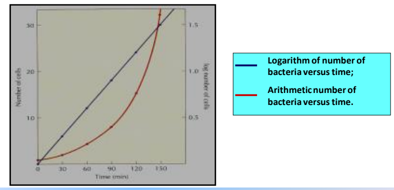
Fragmentation



Exospore Formation

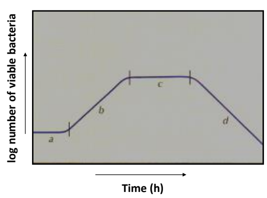
Environmental Systems – Description and Design

Hypothetical bacterial growth curve, assuming that one bacterial cell is inoculated into a medium and divisions occur regularly at 30-min intervals (generation time).



Environmental Systems – Description and Design

Microbial Growth in Batch System



Typical bacterial growth curve;
a: lag phase;
b: log (logarithmic), or exponential phase;
c: stationary phase;
d: death or decline phase.

Environmental Systems – Description and Design

Microbial Growth – Logistic Model:

Let x(t) → Number of Organisms at time 't'
B(x,t) → Birth (Growth) rate → more precisely specific birth (growth) rate
D(x,t) → Death rate → more precisely specific death rate

Number of births in time Δt = B(x,t) x(t) Δt
Number of deaths in time Δt = D(x,t) x(t) Δt
Any other reason for change in number (population), say

Immigration = I(x,t) x(t) Δt
Emigration = E(x,t) x(t) Δt

Prediction is very complex in nature, several factors influence this.

Environmental Systems – Description and Design

Microbial Growth – Logistic Model:

Population growth in time Δt

= x(t+Δt) – x(t) = B(x,t) x(t) Δt + I(x,t) x(t) Δt – D(x,t) x(t) Δt – E(x,t) x(t) Δt

or $$\frac{x(t+\Delta t)-x(t)}{\Delta t} = [B(x,t)+I(x,t)]x(t) - [D(x,t)+E(x,t)]x(t)$$

≅ B.x – D.x ; ***neglecting I & E***

Environmental Systems – Description and Design

Microbial Growth – Logistic Model:

Or as Δt → 0 $\frac{dx}{dt} = Bx - Dx$;

$B = \lambda_1 - \lambda_2 x$,

$D = \mu_1 - \mu_2 x$

B→ Decreasing rate of increase in population
D→ Increasing rate of decrease in population

$$\frac{dx}{dt} = (\lambda_1 - \lambda_2 x)x - (\mu_1 + \mu_2 x)x = (\underbrace{\lambda_1 - \mu_1}_{a})x - (\underbrace{\lambda_2 - \mu_2}_{b})x^2$$

$$= ax - bx^2$$

$$or \quad \frac{dx}{ax - bx^2} = dt \qquad or \quad \frac{dx}{ax} + \frac{b}{a}\frac{dx}{(a-bx)} = dt$$

Environmental Systems – Description and Design

Microbial Growth – Logistic Model:

$$or \quad \frac{1}{a}\int\frac{dx}{x}+\frac{b}{a}\int\frac{dx}{a-bx}=\int dt$$

$$or \quad \ln x-\ln(a-bx)=at+const$$

$$at \quad t=0, x=x_o \ \& \ const=\ln\frac{x_o}{a-bx_o}$$

$$\therefore \quad \ln\left[\frac{x}{a-bx}\right]=at+\ln\left[\frac{x_o}{a-bx_o}\right]$$

Environmental Systems – Description and Design

Microbial Growth – Logistic Model:

$$x=\frac{\left(a/b\right)x_o}{x_o+\left(a/b-x_o\right)e^{-at}} \qquad a/b=\omega$$

$$x=\frac{\omega\, x_o}{x_o+(\omega-x_o)\,e^{-at}}; \quad x_{max}=\omega \quad i.e.\ at\ t=\infty$$

Point of inflection

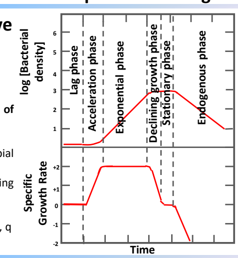
$$\frac{d}{dt}\left(\frac{dx}{dt}\right)=0\Rightarrow\left\{\frac{1}{a}\ln\left[\frac{\omega-x_o}{x_o}\right],\frac{\omega}{2}\right\}$$

Environmental Systems – Description and Design

Microbial Growth and Substrate Utilization

Environmental Systems – Description and Design

Microbial Growth Curve

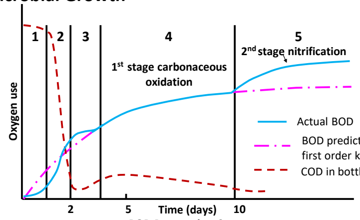


Characteristics Growth Curve of Cultures of Microorganisms

- Microbial Number α Microbial Mass, x
- Food or Substrate or Limiting Growth Element, s
- Specific growth rate, dx/dt/x, μ
- Specific substrate utilization rate, q

Environmental Systems – Description and Design

Microbial Growth



BOD Progression Curve

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Substrate Utilization and Growth Relationship

Specific Substrate Utilization Rate (q);
Specific Growth Rate (μ); and Yield Coefficient (y)

$$\mu=\frac{\left(dx/dt\right)_g}{x};$$

$$y=\frac{dx}{ds};$$

$$q=\frac{ds/dt}{x}=\frac{\frac{ds}{dt}\cdot\frac{dx}{ds}}{\frac{dx}{ds}x}=\frac{dx/dt\,/\,x}{dx/ds}=\frac{\mu}{y}$$

Environmental Systems – Description and Design

Substrate Utilization and Growth Relationship

Total Substrate Utilized = Substrate Utilized for Synthesis + Substrate Utilized (Oxidized) for Energy

$$(\Delta s)_T = (\Delta s)_S + (\Delta s)_E \quad or \quad \left(\frac{\Delta s}{\Delta x}\right)_T = \left(\frac{\Delta s}{\Delta x}\right)_S + \left(\frac{\Delta s}{\Delta x}\right)_E \quad or \quad \frac{1}{y} = \frac{1}{y_s} + \frac{1}{y_E}$$

y_E is not a real value, it indicates that fraction of 's' removed per unit of 'x' which is channeled into energy metabolism.

$$\left(\frac{\Delta s}{\Delta x}\right)_S = 1 \quad or \quad \frac{1}{y_S} = 1$$

$$(\Delta s)_E = (\Delta s)_{Growth\,Energy} + (\Delta s)_{Maintenance\,Energy} = (\Delta s)_{GE} + (\Delta s)_{ME}$$

$$\left(\frac{\Delta s}{\Delta x}\right)_E = \frac{(\Delta s)_{GE} + (\Delta s)_{ME}}{\Delta x} = \frac{1}{y_E}$$

Environmental Systems – Description and Design

Substrate Utilization and Growth Relationship

When -

$$(\Delta s)_{ME} = 0, \quad \left(\frac{\Delta s}{\Delta x}\right)_E = \left(\frac{\Delta s}{\Delta x}\right)_{GE} = \frac{1}{y_E}$$

This represents maximum yield condition because a portion of the 's' that might have been oxidized to provide for Maintenance Energy will now be assimilated into new biomass. Under this condition 'y' is maximum and is termed as true or total growth yield coefficient, "y_T"

$(\Delta s)_{ME} \rightarrow$ Substrate Utilization for Maintenance Energy is proportional to x or,

$$\left(\frac{ds}{dt}\right)_{ME} \propto x \quad or \quad \left(\frac{ds}{dt}\right)_{ME} = bx \rightarrow \text{b Maintenance Energy Coefficient}$$

Environmental Systems – Description and Design

Substrate Utilization and Growth Relationship

Relationship between S-Utilization, True yield Coefficient and Maintenance Energy (ME) Coefficient

(Assumption: ME requirement satisfied from external substrate):

$$(\Delta s)_{U-T} = (\Delta s)_{U-G} + (\Delta s)_{U-E}$$
$$= (\Delta s)_{U-G} + (\Delta s)_{U-GE} + (\Delta s)_{U-ME}$$
$$= (\Delta s)_{U-GF} + (\Delta s)_{U-ME}$$

Environmental Systems – Description and Design

Substrate Utilization and Growth Relationship

In terms of rate:

$$\left(\frac{ds}{dt}\right)_{U-T} = \left(\frac{ds}{dt}\right)_{U-GF} + \left(\frac{ds}{dt}\right)_{U-ME} = \left(\frac{ds}{dt}\right)_{U-GF} + bx$$

$$or \quad \frac{\left(\frac{ds}{dt}\right)_{U-T}}{x} = \frac{\left(\frac{ds}{dT}\right)_{U-GF}}{x} + b = \frac{\frac{1}{y_T}\frac{dx}{dt}}{x} + b;$$

$$\frac{dx}{ds} = y \quad or \quad ds = \frac{dx}{y}$$

$$or \quad q = \frac{\mu}{y_T} + b \quad or \quad \mu = y_T(q - b) \rightarrow (1)$$

Environmental Systems – Description and Design

Relationship between Substrate Utilization, True yield Coefficient and ME Coefficient in Endogenous respiration

Assumption: When the substrate is completely exhausted i.e. stationary phase/declining growth phase, ME requirement is satisfied through endogenous metabolism i.e. the cellular compounds are oxidized to produce the ME for the cell and hence the biomass decreases (auto-oxidation → expensive in terms of energy yield)

To account for decrease in biomass production that is observed when the specific growth rate, μ, decreases, Herbert (1958) suggested that the ME is satisfied through endogenous metabolisms, i.e. cellular components are oxidized.

Environmental Systems – Description and Design

Substrate Utilization and Growth Relationship

[Net Growth] = [Total Growth] – [Biomass Lost due to Endogenous Respiration for ME]

$$\left(\frac{dx}{dt}\right)_{N-g} = \left(\frac{dx}{dt}\right)_{T-G} - \left(\frac{dx}{dt}\right)_{ME}; \quad \left(\frac{dx}{dt}\right)_{ME} \propto x = k_d x$$

$$= \left(\frac{dx}{dt}\right)_{T-G} - k_d x \quad = y_T\left(\frac{dS}{dt}\right)_U - k_d x$$

$$or \quad \frac{\left(\frac{dx}{dt}\right)_{N-g}}{x} = \frac{y_T\left(\frac{ds}{dt}\right)_U}{x} - k_d$$

Environmental Systems – Description and Design

Substrate Utilization and Growth Relationship

$$or \quad \mu = y_T q - k_d \quad or \quad q = \frac{\mu}{y_T} + \frac{k_d}{y_T} \rightarrow (2)$$

Where 'k_d' is microbial decay coefficient or ME coefficient during endogenous respiration → similar to 'b' but not same as 'b'.

$$q = \frac{\mu}{y_T} + b \quad or \quad \mu = y_T (q - b) \rightarrow (1)$$

Compare (1) & (2) → they are similar, $b = {k_d}/{y_T}$; however specific oxygen utilization will be different.

$$y_{Observed} \quad or \quad y_{real} \quad or \quad y_{Actual}$$

'y' is a variable depending upon the Growth Stage

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Environmental Systems – Description and Design

Substrate Utilization and Growth Relationship

$$y_{Observed} \quad or \quad y_{real} \quad or \quad y_{Actual}$$

'y' is a variable depending upon the Growth Stage

$$y_{Obs} = \frac{\left(\frac{dx}{dt}\right)_g}{\left(\frac{ds}{dt}\right)_U} = \frac{\frac{\left(\frac{dx}{dt}\right)_g}{X}}{\frac{\left(\frac{ds}{dt}\right)_U}{x}} = \frac{\mu}{q} = \frac{\mu}{\frac{\mu}{y_T} + \frac{k_d}{y_T}} = \frac{y_T}{1 + {k_d}/{\mu}}$$

$$or \quad y_{Obs} = \frac{y_T}{1 + {k_d}/{\mu}} = \frac{y_T}{1 + k_d \theta_c} \rightarrow (3)$$

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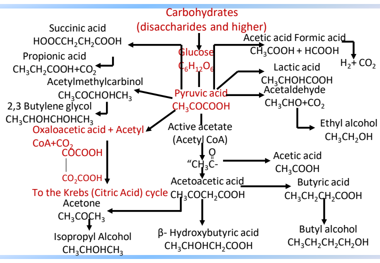
Representation of the Pivotal Nature of Pyruvic Acid



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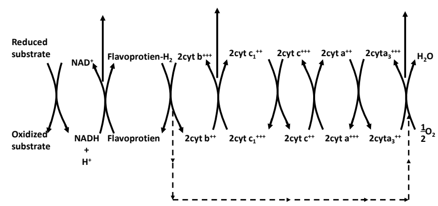
Heterotrophic Aerobic Bacteria Energy for synthesis of ATP



Electron Transport System Common to Most Bacteria

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Applications

- Selection of Microorganisms
  - Heterotrophic or Autotrophic
  - Aerobic or Anaerobic
  - Chemosynthetic or Photosynthetic
- Growth Rate/Condition of Microbes
  - High Growth Rate or Auto Oxidation/Endogenous Phase
- Physical and Chemical Environment
  - Temperature, pressure
  - pH, nutrition, toxic substances
- Housing and Mixing
  - Suspended/immobilized or fixed or attached, homogenous/heterogeneous, stratified/un-stratified, uniform/non-uniform, steady/unsteady
- Ecology
  - Competition, symbiosis, predation, etc.
- System Performance Criteria
  - Removal, sludge production, gas production, energy requirement, etc.

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Applications

- Suspended Growth Systems - Activated Sludge Process and its Modifications
- Immobilized/Attached Growth or Fixed Film Systems - Trickling Filter/Rotating Biological Contactors

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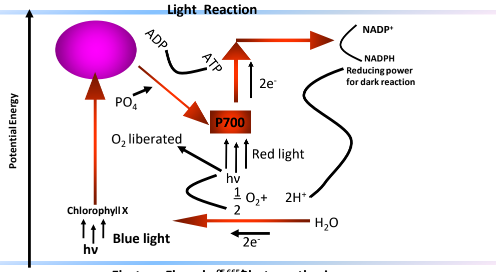
Photosynthesis



Electron Flow during Photosynthesis

Photosynthesis

Dark Reaction

6 ribulose 1, 5-diphosphate + $6CO_2$ + 18ATP + 12NADPH + $12H^+$

↓

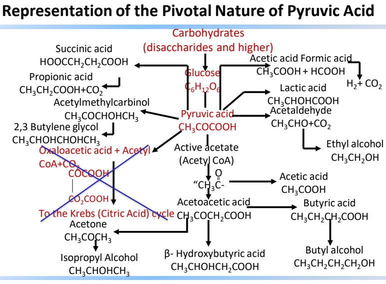
6 ribulose 1,5-diphosphate + hexose + $18P_i$ + 18ADP+ 12NADP

Electron Flow during Photosynthesis

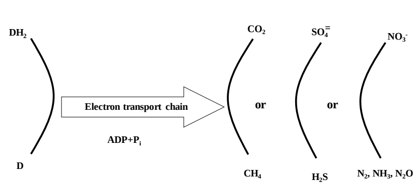
Applications

- **Oxidation Ponds** – Suspended Growth Systems
- **Facultative Ponds** – Suspended Growth Systems
- **Anaerobic Ponds** – Suspended Growth Systems

Representation of the Pivotal Nature of Pyruvic Acid



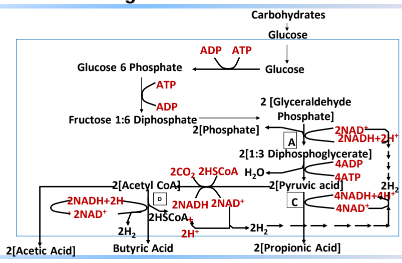
Electron Transport Chain for Anaerobic Respiration



Applications

- Anaerobic Systems – Denitrification
- Anaerobic Systems – Sulphate Reduction
- Anaerobic Systems – Methanogenesis

Anaerobic Degradation



Standard Gibbs Free Energy Values (ΔG^O) for Conversion of Ethanol, Propionate and Butyrate to Methane

Source: McCarty and Smith, 1986

S No.	Reaction		ΔG^O(KJ)
1	**Ethanol Conversion**		
	Ethanol	$CH_3CH_2OH + H_2O \rightleftharpoons CH_3COO^- + H^+ + 2H_2$	+9.65
	Hydrogen	$2H_2 + ½\, CO_2 \rightleftharpoons ½\, CH_4 + H_2O$	-65-37
	Acetate	$CH_3COO^- + H^+ \rightleftharpoons CH_4 + CO_2$	-35.83
	Net	$CH_3CH_2OH \rightleftharpoons 3/2\, CH_4 + ½\, CO_2$	-91.55
2	**Propionate Conversion**		
	Propionate	$CH_3CH_2COO^- + 2H_2O \rightleftharpoons CH_3COO^- + 3H_2 + CO_2$	+71.87
	Hydrogen	$3H_2 + ¾\, CO_2 \rightleftharpoons ¾\, CH_4 + 3/2\, H_2O$	-98.06
	Acetate	$CH_3COO^- + H^+ \rightleftharpoons CH_4 + CO_2$	-35.83
	Net	$CH_3CH_2COO^- + H^+ + ½\, H_2O \rightleftharpoons 7/4\, CH_4 + 5/4\, CO_2$	-62.22

Standard Gibbs Free Energy Values (ΔG^O) for Conversion of Ethanol, Propionate and Butyrate to Methane

Source: McCarty and Smith, 1986

S No.	Reaction		ΔG^O(KJ)
3	**Butyrate Conversion**		
	Butyrate	$CH_3CH_2CH_2COO^- + 2H_2O \rightleftharpoons 2CH_3COO^- + 2H_2 + H^+$	+48.30
	Hydrogen	$2H_2 + 1/2\, CO_2 \rightleftharpoons 1/2\, CH_4 + H_2O$	-65.37
	Acetate	$2\, CH_3\, COO^- + 2\, H^+ \rightleftharpoons 2CH_4 + 2CO_2$	-71.66
	Net	$CH_3CH_2CH_2COO^- + H_2O + H^+ \rightleftharpoons 5/2\, CH_4 + 3/2\, CO_2$	-88.73

Some Redox Half-reactions for Degradation of Selected Organics during Anaerobic Treatment of Industrial, Municipal, and Agricultural Wastes

Source: Thauer *et al*, 1977

S No.	Reaction	ΔG^O(KJ)
Oxidations (electron donating reactions)		
1	Propionate $\rightleftharpoons$ Acetate:	
	$CH_3COO^- + 3\, H_2O \rightleftharpoons CH_3COO^- + H^+ + HCO_3^-$	+76.1
2	Butyrate $\rightleftharpoons$ Acetate:	
	$CH_3CH_3COO^- + 2H_2O \rightleftharpoons 2\, CH_3COO^- + H^+ + 2H_2$	+48.1

Some Redox Half-reactions for Degradation of Selected Organics during Anaerobic Treatment of Industrial, Municipal, and Agricultural Wastes

Source: Thauer *et al*, 1977

S No.	Reaction	ΔG^O(KJ)
Oxidations (electron donating reactions)		
3	Ethanol $\rightleftharpoons$ Acetate:	
	$CH_3CH_2OH + H_2O \rightleftharpoons CH_3COO^- + H^+ + 2\, H_2$	+9.6
4	Lactate $\rightleftharpoons$ Acetate	
	$CH_3CHOHCOO^- + 2H_2O \rightleftharpoons CH_3COO^- + HCO_3^- + H^+ + 2H_2$	-4.2
5	Acetate $\rightleftharpoons$ Methane:	
	$CH_3COO^- + H_2O \rightleftharpoons HCO_3^- + CH_4$	-31.0

Some Redox Half-reactions for Degradation of Selected Organics during Anaerobic Treatment of Industrial, Municipal, and Agricultural Wastes

Source: Thauer *et al*, 1977

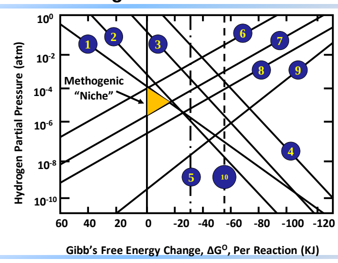
S No.	Reaction	ΔG^O(KJ)
Respirative (electron accepting reactions)		
6	$HCO_3^- \rightleftharpoons$ Acetate:	
	$2HCO_3^- + 4\, H_2 + H^+ \rightleftharpoons CH_3COO^- + 4\, H_2O$	-104.6
7	$HCO_3^- \rightleftharpoons$ Methane:	
	$HCO_3^- + 4\, H_2 + H^+ \rightleftharpoons CH_4 + 3\, H_2O$	-135.6
8	Sulfate $\rightleftharpoons$ Sulfide:	
	$SO_4^{-2} + 4H_2 + H^+ \rightleftharpoons HS^- + 4H_2O$	-151.9

Some Redox Half-reactions for Degradation of Selected Organics during Anaerobic Treatment of Industrial, Municipal, and Agricultural Wastes

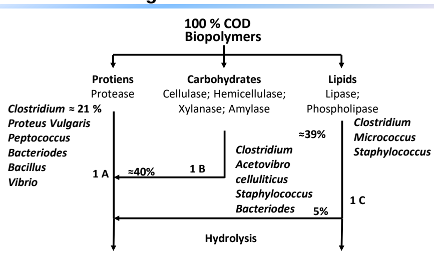
Source: Thauer *et al*, 1977

S No.	Reaction	ΔG^O(KJ)
	Respirative (electron accepting reactions)	
9	Sulfite ⇌ Sulfide	
	$SO_3^{-2} + 3\,H_2 + H^+ \rightleftharpoons HS^- + 3\,H_2O$	-286.5
10	$CH_3COO^- + SO_4^{-2} + H^+ \rightleftharpoons 2\,HCO_3^- + H_2S$	-59.9
11	Nitrate ⇌ Ammonia:	
	$NO_3^- + 4\,H_2 + 2\,H^+ \rightleftharpoons NH_4^- + 3\,H_2O$	-599.6
12	$CH_3COO^- + NO_3^- + H^+ + H_2O \rightleftharpoons 2\,HCO_3^- + NH_4$	-511.4
13	Nitrate ⇌ Nitrogen gas:	
	$2\,NO_3^- + 5\,H_2 + 2\,H^+ \rightleftharpoons N_2 + 6\,H_2O$	-1120.5

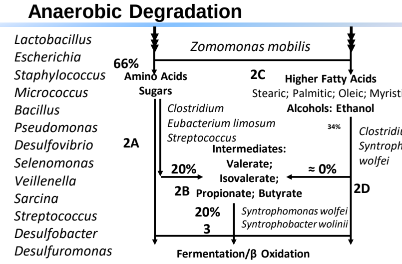
Anaerobic Degradation



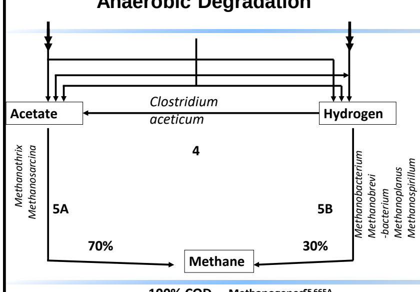
Anaerobic Degradation



Anaerobic Degradation



Anaerobic Degradation



Percentages indicate substrate flow (stoichiometrically) in the form of COD. Only the net flow of substrate (degradation minus biomass formed) through cell external pools is indicated. Numbers in boxes identify different pathways.

Breakdown of Organic Polymers alongwith Bacterial Species involved in Methanogenesis.

Sources: Gujer and Zehnder, 1983 and Stronach et al., 1986).

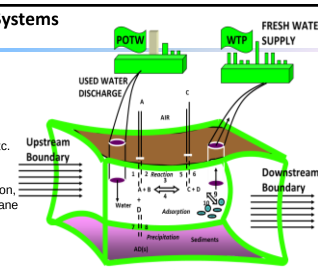
Analysis of Environmental Systems

Phases:
Solid; Liquid and/or Gaseous

Species:
Dissolved; Precipitated and/or Gaseous

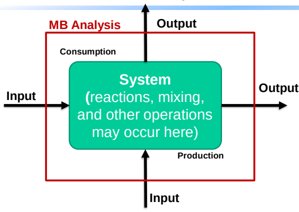
Processes:
Physical: Advection, Diffusion, Settling, etc.
Chemical: Reactions, Precipitation, Dissolution, etc.
Physico-chemical: Coagulation-Flocculation, Filtration, Absorption, Adsorption, Membrane Filtration, etc.
Biological: Degradation, Synthesis, etc.

Reactions:
Homogeneous (3 & 4)
Heterogeneous (1,2, 5 to 10)



A Natural Environmental Macroscale System

Mass Balance Principle – Law of Conservation of Mass

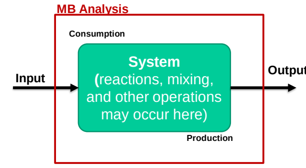


System/Reactor:
- Completely Mixed
- Plug Flow
- Neither Completely Mixed nor Plug Flow

Net Change in system = Input – Output + Production – Consumption

Mass Balance Principle – Law of Conservation of Mass

City Example



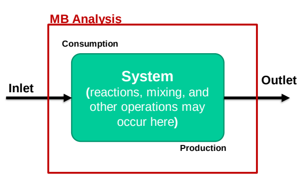
- Immigration = +50
- Emmigration = -3
- Born = +100
- Death = -25

What is the "Net Change" in the city?

= 50 – 3 + 100 – 25 = 122

Mass Balance Principle – Law of Conservation of Mass

Example of a Reactor

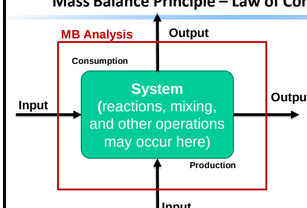


- MB in system
- Input of A = 100 kg
- Production = 0 kg
- Consumption = 50 kg
- Output = 25 kg

What is the "Net Change" in the System?

= 100 + 0 – 50 – 25 = 25 kg accumulated in the system

Mass Balance Principle – Law of Conservation of Mass



System/Reactor:
- Completely Mixed
- Plug Flow
- Neither Completely Mixed nor Plug Flow

Net Rate of Change in the System

= Rate of Input – Rate of Output + Rate of Production – Rate of Consumption

Mass Balance Principle – Law of Conservation of Mass

City Example

- Immigration = +50/annum
- Emigration = -3/annum
- Born = +100/annum
- Death = -25/annum

Example of a Reactor

- Rate of Input of A = 100 kg/d
- Production = 0 kg/d
- Consumption = 50 kg/d
- Output = 25 kg/d

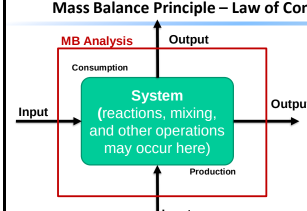
What is the "Net Rate of Change" in the city?

= 50 – 3 + 100 – 25 = 122

What is the "Net Rate of Change" in the System?

= 100 + 0 – 50 – 25 = 25 kg accumulated in the system

Mass Balance Principle – Law of Conservation of Mass



Net Rate of Change in the System

= Rate of Input – Rate of Output
+ Rate of Production
– Rate of Consumption

$$V\left[\frac{\partial C}{\partial t}\right]_{Net\ Change} = Q.Ci - Q.Ce$$

$$+V\left[\frac{\partial C}{\partial t}\right]_{Production/Addition}$$

$$-V\left[\frac{\partial C}{\partial t}\right]_{Consumption/Removal}$$

Control of Microorganisms: Principles and Physical Agents

Overview:

- Effective management of microorganisms in the laboratory, the home, the hospital and the industrial setting depends upon a knowledge of how to control (i.e. kill, inhibit, or remove) microorganisms in an environment.
- Various physical and chemical agents can be used to keep microorganisms at acceptable levels.
- Selection of the best agent depends in part on whether you want to kill or remove all of the microbes present, kill only certain types, or merely prevent those already present from multiplying.
- Some familiar uses of physical agents to control microorganisms include the thorough cooking of poultry and meat to kill *Salmonella* bacteria, and the pasteurization of milk to destroy bacteria that can cause tuberculosis and typhoid fever.

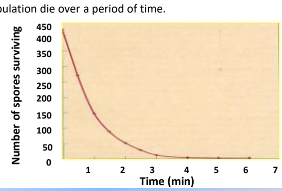
Control of Microorganisms: Principles and Physical Agents

- Fundamentals of Microbial Control
  - Substances that either kill microorganisms or prevent their growth are called *antimicrobial* agents. More specifically, these are *antibacterial*, *antiviral, antifungal,* and *antiprotozoan* agents, depending on the kind of microorganism affected.
  - Antimicrobial agents that kill microorganisms are called as microbicidal agents. The names bactericidal, virucidal, and fungicidal indicate the type of microorganism killed.
  - Killing all the microorganism present in a material including any spores, is called sterilization.
  - Agents that merely inhibit the growth of microorganisms are called microbiostatic agents. Again, more specific names can be used, such as bacteriostatic or fungistatic.
  - Antimicrobial agents may be either physical agents or chemical agents.

Control of Microorganisms: Principles and Physical Agents

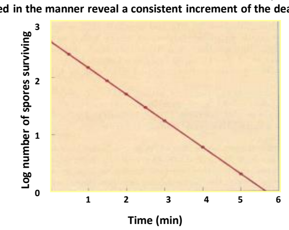
Pattern of death in a Microbial Population

The arithmetic death curve of the bacterial spores exposed to a 5% phenol solution at a constant temperature illustrates that the spores in the population die over a period of time.



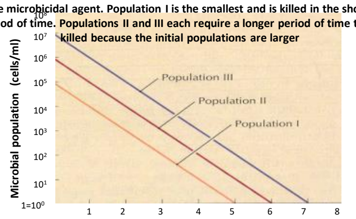
Control of Microorganisms: Principles and Physical Agents

The logarithmic death curve is based on the same data as the preceding curve. Data expressed in the manner reveal a consistent increment of the deaths per unit time.



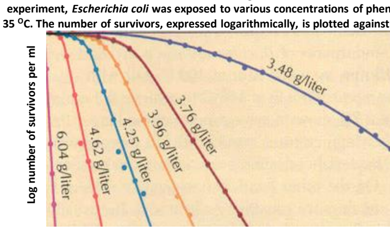
Control of Microorganisms: Principles and Physical Agents

Graph showing death rates of three different microbial populations exposed to same microbicidal agent. Population I is the smallest and is killed in the shortest period of time. Populations II and III each require a longer period of time to be killed because the initial populations are larger



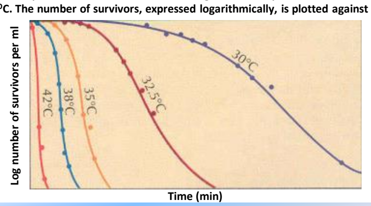
Control of Microorganisms: Principles and Physical Agents

Effect of concentration of an anti-microbial agent on bacterial death. In this experiment, *Escherichia coli* was exposed to various concentrations of phenol at 35 °C. The number of survivors, expressed logarithmically, is plotted against time.



Control of Microorganisms: Principles and Physical Agents

An increase in temperature decreases bacterial survival when the concentration of the anti-microbial agent remains the same. In this experiment, *Escherichia coli* was exposed to phenol at a concentration of 4.62 g/liter at temperatures between 30 and 42 °C. The number of survivors, expressed logarithmically, is plotted against time.



Control of Microorganisms: Principles and Physical Agents

Conditions that Affect Antimicrobial Activity

- When microbicidal agents are used for some practical application, there can be great variation in the conditions affecting each situation.
- Some important variables to consider when accessing the effectiveness of a microbicidal agent are:

1. Size of microbial population. Large populations take longer to kill than small populations.
2. Intensity or concentration of the microbicidal agent. The lower the intensity or concentration, the longer it takes to kill a microbial population.
3. Time of exposure to the microbicidal agent. The longer the time, the greater the number of cells killed.
4. Temperature at which the microorganisms are exposed to the microbicidal agent. In general, the higher the temperature, the more quickly a population is killed.
5. Nature of the material containing the microorganisms.
6. Characteristics of the microorganisms which are present. Microorganisms vary considerably in their resistance to physical and chemical agents. For example, many Gram-positive species are more resistant to heat than Gram-negative species; some chemicals are more effective against Gram-positive species than they are against Gram-negative species.

Control of Microorganisms: Principles and Physical Agents

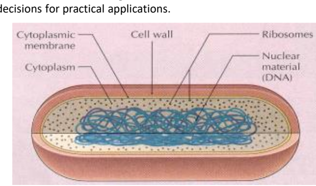
- The use of high temperatures is one of the most effective and widely utilized means of killing microorganisms. Heat may be applied in either a moist condition (steam or water) or in a dry condition. The most extreme use of high temperatures to kill microorganisms is incineration (burning)

- Moist Heat/Dry heat
- Low Temperatures

Control of Microorganisms: Principles and Physical Agents

Mechanisms of Microbial Cell Damage

Antimicrobial agents inhibit or kill microorganisms by damaging certain structures of the cells, such as the cell wall or the cytoplasmic membrane, or substances within the cytoplasm, such as enzymes, ribosomes, or nuclear material. Knowledge of the mode of action of an anti microbial agent is of the value in making decisions for practical applications.

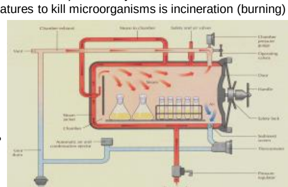


Control of Microorganisms: Principles and Physical Agents

The use of high temperatures is one of the most effective and widely utilized means of killing microorganisms. Heat may be applied in either a moist condition (steam or water) or in a dry condition. The most extreme use of high temperatures to kill microorganisms is incineration (burning)

- Moist Heat
- Dry heat

Low Temperatures?



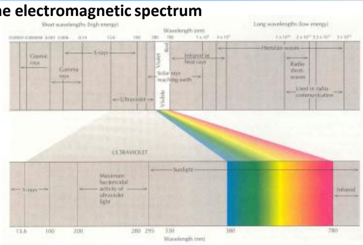
Control of Microorganisms: Principles and Physical Agents

Radiation

- Electromagnetic radiation is energy in the form of electromagnetic waves transmitted through space or through a material. Electromagnetic radiation is classified according to its wavelength, with radio waves having the longest wavelength and cosmic rays having the shortest.
- The energy content of the radiation is inversely related to the wavelength: shorter the wavelength, the greater the energy content.
- High-energy radiation includes gamma rays, x-rays, and ultravoilet lights. Theses can kill living cells, including microorganisms.
- Some form of electro magnetic radiation ionize molecules, while others do not.

Control of Microorganisms: Principles and Physical Agents

The electromagnetic spectrum



Control of Microorganisms: Principles and Physical Agents

- Radiation
  - Ionizing radiation
    - High energy electron beams, gamma rays, and x-rays have sufficient energy to cause ionization of molecules: they drive away electrons and split the molecules into atoms or groups of atoms.
  - Non ionizing radiation
    - Ultravoilet (UV) radiation has a wavelength range of 136 to 400 nanometers (nm).
    - Rather than ionize a molecule, UV light excites its electron causing the molecule to react differently from nonirradiated molecules.
- Filtration
  - Membrane filters
- Desiccation

Control of Microorganisms: Chemical Agents

Overview

- There are hundreds of different chemical products available for the control of microorganisms.
- Certain antimicrobial chemicals kill microorganisms, while other inhibit their growth.
- Some can do either, depending on the concentration at which they are used.
- Some are active against a large number of species and are characterized as having a broad spectrum of activity, while other chemical agents may affect only a few species.
- There is not a single chemical agent that is optimal for all the purposes.

Control of Microorganisms: Chemical Agents

Terminology of Chemical Antimicrobial Agents

- **Sterilant:** Sterilization is the process of destroying or removing all forms of microbial life from an object or a specimen. Thus a sterile item is one which is free of all living organisms, and a sterilant is a chemical agent that accomplishes sterilization.
- **Disinfectant:** A disinfectant is a chemical substance that kills the vegetative forms of microorganisms that can cause disease but does not necessarily kill there spores. The term normally refers to substances used on inanimate objects. Disinfection is the process of using such an agent to destroy infections microorganisms
- **Germicide:** A chemical agent that kills the vegetative forms of microorganisms, but not necessarily their spores, is called a germicide. In practice, it is almost synonymous with a disinfectant; however the microorganisms killed by a germicide are not necessarily disease-producing microbes.

Control of Microorganisms: Chemical Agents

Terminology of Chemical Antimicrobial Agents

- **Antiseptic:** An antiseptic is a chemical agent, usually applied to the surface of the body, that prevents microorganisms from multiplying.
- **Sanitizer:** Public health guidelines mandate that, in certain settings, microbial populations should not exceed specific numbers. Compliance with this rules is accomplished by using a sanitizer, an agent that kills 99.9 percent of microorganisms contaminating an area.

Control of Microorganisms: Chemical Agents

Characteristics of an Ideal Chemical Agent:

- Antimicrobial activity
- Solubility
- Stability
- Lack of toxicity
- Homogeneity
- Minimum inactivation by extraneous material
- Activity at ordinary temperatures
- Ability to penetrate
- Material safety
- Deodorizing ability
- Detergent ability
- Availability and low cost

Control of Microorganisms: Chemical Agents

Major groups of Disinfectant and Antiseptics

- Chemical substances used for disinfection or antisepsis are divided into several major groups: Phenol and phenolic compounds, alcohols, the halogens iodine and chlorine, heavy metals and their compounds, and detergents
  - **Phenol and Related Compounds:**
    - Phenol, also called carbolic acid, has the distinction of being one of the first chemical agents used as an antiseptic
  - **Mode of action of phenol and related compounds:**
    - Phenol and phenolic compounds damage microbial cells by altering the normal selective permeability of the cytoplasmic membrrane, causing leakage of vital intracellular substances.
    - These chemicals also denature and inactivate proteins such as enzymes.
    - They may be either bacteriostatic or bactericidal, depending on the concentration used.

Control of Microorganisms: Chemical Agents

Major groups of Disinfectant and Antiseptics

- **Alcohols:**
  - In concentrations between 70 and 90 %, solutions of ethyl alcohol (ethanol), CH_3CH_2OH, are effective against the vegetative forms of microorganisms. But ethyl alcohol can not be relied upon to sterlize an object because it does not kill bacterial endospores.
  - Methyl alcohol, or methanol (CH_3OH) X ?
- **Mode of action of alcohols:**
  - Alcohols are protein denaturants, which accounts to a large extent for their antimicrobial activity.
  - Alcohols are also lipid solvent, thus damaging the lipid structure within microbial cell membranes.
  - In addition, some of their effectiveness as surface disinfectant can be attributed to their cleansing or detergent action, which helps in the mechanical removal of microorganisms.

Control of Microorganisms: Chemical Agents

Major groups of Disinfectant and Antiseptics

Halogens

- The halogens are strong oxidizing agents and by virtue of this property are highly reactive and destructive to vital compounds within the microbial cell.
- **Iodine and Iodine Compounds**

  Mode of action of iodine and its compounds.

  - A strong oxidizing agent, iodine can destroy essential metabolic compounds of microorganisms through oxidation. The ability of iodine to combine with the amino acid tyrosine results in the inactivation of enzymes and other proteins.

Control of Microorganisms: Chemical Agents

Major groups of Disinfectant and Antiseptics - Halogens

- Chlorine and chlorine compounds:
  - Mode of action of chlorine and its compounds:
  - The antimicrobial action of chlorine and its compounds is due to the hypochlorous acid (HClO) formed when free chlorine is added to water:

    $$Cl_2 + H_2O \rightleftarrows HCl + HClO$$

  - When added to water, hypochlorites and chloramines undergo hydrolysis, giving rise to hypochlorous acid. This acid undergoes further change, giving rise to nascent oxygen (O):

    $$HClO \rightleftarrows HCl + O$$

  - Nascent oxygen is a powerful oxidizing agent that can severely damage vital cellular substances. Chlorine may also combine directly with cellular proteins and destroy their biological activity.

Control of Microorganisms: Chemical Agents

Major groups of Disinfectant and Antiseptics

- Heavy Metals and their Compounds
- Detergents

Control of Microorganisms: Chemical Agents

Chemical Sterilant

- Chemical sterilant are particularly useful for the sterilization of heat-sensitive medical supplies, such as plastic blood transfusion or donor sets, plastic syringes, and catheterization equipment.
- The major chemical sterilant in use are
  - Ethylene oxide
  - β - propiolactone
  - Glutaraldehyde
  - Formaldehyde.

End of Part 6: Thank You

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